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ABSTRACT

This volume is one of a series discussing instrumentation for environmental monitoring. Each volume contains an overview of the basic problems, comparisons among the basic methods of sensing and detection, and notes that summarize the characteristics of presently available instruments and techniques. The text of this survey discusses the instrumentation presently available to provide quantitative monitoring for fresh water and estuarine water. Techniques which may be developed into instrumentation are also discussed. In addition, recommendations for improved or new instrumentation are included. Each section of this volume addresses a particular pollutant or parameter and contains an introduction discussing relevant background information and a detailed critique of instrumentation techniques. Information pertinent to the individual instruments is given in the instrument notes. Topical areas include: metals; halides and cyanide; biological parameters; phenolics; petrochemicals; radiation; and physical parameters. (CS)

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ABSTRACT

A comprehensive survey of instrumentation for environmental monitoring is being carried out by the Lawrence Berkeley Laboratory originally under a grant from the National Science Foundation and now by the Energy Research and Development Administration. Instruments being investigated are those useful for measurements in Air Quality, Water Quality, Radiation, and Biomedicine related to environmental research and monitoring. Consideration is given to instruments and techniques presently in use and to those developed for other purposes but having possible applications to this work. The results of the survey are given as (a) descriptions of the physical and operating characteristics of available instruments, (b) critical comparisons among instrumentation methods, and (c) recommendations of promising methodology and development of new instrumentation.

The survey material will be compiled in six loose-leaf binders which can be periodically updated.

Volume	Parts	Category
1	1 and 1A	Air Monitoring, Gases
1	2	Air Monitoring, Particulates
2		Water Monitoring
3		Radiation Monitoring
4		Biomedical Monitoring

INDEXING METHOD

The sections of the survey are indexed by a series of mnemonic descriptors. The caption in the upper right-hand corner of each page provides the necessary filing information. The first three-character descriptor indicates the category of monitoring:

Category	Mnemonic descriptor
Air Monitoring	AIR
Water Monitoring	H2O
Radiation Monitoring	RAD
Biomedical Monitoring	BIO

The second descriptor indicates the type of parameter under discussion. For example, oxygen monitoring instruments are identified by "H2O-DO." A list of descriptors is given in the contents.

The third descriptor is used to identify the specialized topic, type of sampling or use, for example, "H2O-PES, Laboratory" signified laboratory instruments suitable for monitoring pesticides.

The manufacturer or developing laboratory is indicated as the fourth descriptor. Additional instrument notes in this category, parameter, and use by this manufacturer, are indicated by numerals after the manufacturer's name.

The last descriptor is the date the note was first issued. Revised notes bear a new date. Descriptions of equipment bearing a new model number will be issued as additional notes.

PROLOGUE

"I often say that when you can measure what you are speaking about and express it in numbers you know something about it, but when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meager and unsatisfactory kind...it may be the beginning of knowledge, but you have scarcely, in your thoughts, advanced to the stage of science whatever the matter may be."

Lord Kelvin, 1883

The wilderness and the parched land shall be glad; and the desert shall rejoice, and blossom as the rose. It shall blossom abundantly, and rejoice, even with joy and singing;....And the parched land shall become a pool, and the thirsty ground springs of water;....

Isaiah 35: 1,2,7

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PREFACE

It is essential to the nation's program of environmental improvement that accurate and efficient measurements be made of the parameters affecting the environment in which we live and work. In many important areas the present state of the art of instrumentation for environmental monitoring is inadequate. There are many reasons for this inadequacy; more relevant, however, is the question: Where are we now and where do we go from here? The Lawrence Berkeley Laboratory, under grants from the National Science Foundation and the U.S. Energy Research Development Administration, is conducting a survey of instrumentation suitable for the measurement of the quality of our environment. The results of the survey appear in four volumes which discuss monitoring of air, water, and radiation, and treat biomedical problems due to environmental causes.

Air Monitoring, Volume 1, primarily considers the chemical parameters known to contribute (or suspected of contributing) to environmental degradation. Physical parameters, usually recorded to establish standard conditions of measurement, are also included.

Water Monitoring, Volume 2, deals with instrumentation suitable for fresh water and estuarine water; coastal and off-shore oceanic waters have been excluded from the survey. Chemical and biological contaminants have been included as well as physical parameters.

Radiation Monitoring, Volume 3, considers both ionizing radiation and non-ionizing radiation. A description of the type of radiation present at various sources of radiation is followed by sections containing a discussion and the specifications for the instrumentation used to monitor its radiation. The non-ionizing sections describe instrumentation used to monitor microwave, laser, and ultraviolet radiation in the environment.

Biomedical Instrumentation, Volume 4, deals with those parameters which affect human, animal and plant life presently considered to arise from environmental problems. Hospital instrumentation is not included. Biomedical problems arising from contamination of the air or water are discussed here, e.g., in the mercury section an overview describes the sources, metabolism, food chain and genetic effects, followed by a description of the methods for detecting mercury in biological samples.

A number of environmental contaminants are well identified, others are at present only suspect, still others are potentially insulting to the ecological balance, and the effects of some substances are unknown. Upon the advice of recognized authorities, the effort expended in compiling this survey has been distributed in proportion to the severity of the problem. If problems are well identified and existing instrumentation is considered satisfactory, presently available instruments are emphasized. If current methods of detection are inadequate --because, for example, of insensitivity, the time consumed in making the measurement or the ambiguity resulting from interfering parameters --present methodology is surveyed and new methods of detection and analysis are explored. Recommendations are made for development and exploitation of techniques that are employed in other disciplines and appear to be applicable in the environmental field.

Each volume contains (a) an overview of the basic problems, (b) comparisons among the basic methods of sensing and detection, and (c) instrument notes that summarize the characteristics and evaluate the presently available instruments and techniques. Steps that should be taken to alleviate the problems are recommended if appropriate.

Contact has been made with the staffs of Federal, state, university, regional and local laboratories as well as with manufacturers interested in instrumentation for environmental monitoring. Due to the nation-wide concern in this field, it is obvious that not all the experienced professionals in any given specialty could be contacted; however, as the survey continues, an endeavor will be made to utilize all the experience and expertise that comes to the attention of the group.

This survey deals predominantly with instrumentation which is available commercially from U.S. sources. The information is derived from manufacturers' catalogs and specifications, the periodic literature, and scientific and engineering reports. Instrumentation from outside the U.S. has been included whenever it has been found to be widely used or merits attention by our readers because of some particular characteristic.

The survey has been compiled from the aforementioned information sources. The limited scope of this program, however, has not allowed the in-house evaluation of operating instruments at this laboratory.

It is realized that no survey can be exhaustive and complete. If any existing or potentially useful instrument or technique has been omitted, it is urged that information about it be communicated to the Environmental Instrumentation Group at once.

It is important to state that the explicit function of this survey is to aid in, but not to be the sole information relied upon in, the choice of instrumentation. Manufacturers' information and the periodic literature in particular must be considered by any potential user.

The technical information in this survey has been compiled from the best available sources and is believed to be correct. The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products. The opinions expressed herein represent the opinions of the LBL Environmental Instrumentation Group and do not necessarily express the opinion of the National Science Foundation, the Energy Research and Development Administration or the University of California.

Dick A. Mack
Environmental Instrumentation Group

WATER MONITORING INSTRUMENTATION

I. INTRODUCTION

A. CATEGORIES OF WATER

Water ranks along with air among our most valuable natural resources. The Earth has been endowed with an ideal purification system through the evaporation-precipitation cycle; unfortunately, however, due to population pressures, economic tradeoffs and human carelessness, water often reaches the ultimate user in a form far less pure than raindrops or melted snow. As McKee and Wolf point out in terms as appropriate today as ten years ago: (Ref. 1).

> "The domestic water-supply industry is caught between two strong trends in water quality. On the one hand, domestic and industrial customers are demanding improved quality and greater uniformity in the water delivered at the tap... On the other hand, the sources of raw water have been deteriorating under the inexorable impacts of modern civilization and may be expected to get worse in future years. The waterworks industry, therefore, must produce a better and more uniform product while drawing upon a poorer and less predictable source of supply. Fortunately, there are many recent improvements in technology that are capable of bridging the widening gap in quality between raw and finished waters. One of the greatest needs today in water-supply technology is reliable quantitative information relative to the potential harmful effects of trace substances in raw and treated water."

The purpose of this Survey is to describe the instrumentation which is presently available to provide the quantitative monitoring information on water today. Techniques which may be developed into instrumentation are also discussed. In addition, recommendations for improved or new instrumentation are included.

Each section of this volume on a particular pollutant or parameter will contain an introduction discussing relevant background information. This will be followed by a detailed critique of instrumentation techniques. Information pertinent to the individual instruments is given to the Instrument Notes. Readers should consult the Instrumentation techniques section for general remarks as well as the Instrument Note for that instrument.

Water has been studied in a variety of ways. In general, studies concerned with water quality subdivide the subject into several categories depending upon the approach taken by the studies. Standard Methods for the Examination of Water and Wastewater (Ref. 2) divides water into two main categories: 1) Natural and treated waters in the absence of gross pollution and 2) Polluted and wastewaters including bottom sediments and sludges. The 1972 Annual Book of ASTM Standards, Part 23, Water; Atmospheric Analysis (Ref. 3) considers Industrial Water and Industrial Wastewater. The Report of the Committee on Water Quality Criteria (Ref. 4) further divides water into five general areas of use: 1) Recreation and Aesthetics, 2) Public Water Supplies, 3) Fish, other Aquatic Life and Wildlife, 4) Agriculture and 5) Industry.

Instrumentation discussed in this Survey will be considered as that suitable for monitoring three categories of water:

1) Fresh Water includes raw or treated water either for domestic, industrial or agricultural use. Gross pollution is not expected to be observed in this category of water.

2) Waste Water includes domestic and industrial wastewater, effluent from waste treatment plants and other polluted waters, as well as bottom sediments and sludges.

3) Saline Water includes brackish waters normally found in estuaries. Brackish waters contain from 1,000 ppm to about 10,000-15,000 ppm total dissolved solids, chiefly sodium, calcium, magnesium, sulfate, chloride and bicarbonate. Nitrates, fluorides and potassium are found in smaller amounts (Ref. 5). Saline water contains 10,000 to 33,000 mg/l of dissolved salts.

Statistics

Only about 0.6% of the 326 million cubic miles of total water found on the earth is on land; the remaining 99.4% is in the seas and polar ice caps (Ref. 5). Of the 2 million cubic miles of the water on land, about one million is found in the first half-mile of the earth's crust, and an almost equal amount in the next mile and a half. Only about 1% is in saline lakes, about 0.1% in all rivers, and less than 0.001% in the atmosphere.

In the U.S. there are more than 3 million miles of streams, 88,000 miles of tidal shoreline and millions of ponds, lakes and bayous. Total daily water use in the U.S. in 1970 was 385 billion gallons (Ref. 6) of which 121 billion (31%) were for steam electric utilities, 119 billion (31%) were for irrigation, 56 billion (15%) were for industrial, commercial and government agencies, 27 billion (7%) were for public water utilities and the remaining 16% for other uses. In 1900 the total water used was only 40 billion gallons; by 1980 the figure is expected to rise to 443 billion gallons.

For many years pure water was almost taken for granted; now, however, the impact of pollution is beginning to be felt. The total outlay for water pollution control in the U.S. in 1969 was 3 billion dollars; by 1974 the amount is expected to exceed 4 billion (Ref. 6). The following section discusses the areas where problems arise.

B. DELETERIOUS EFFECTS

Water should not contain impurities in such concentrations as to be a health hazard to the consumer. Impurities in this sense may be either biological or chemical, with the latter sometimes the result of the former. The solubilization of elemental mercury by microbiological action to form the highly toxic methyl mercury is an example. The analytical or monitoring problem in this case, as in others such as bacterial and algal toxins, is usually chemical in nature. In some instances, however, especially in assessing multicomponent industrial wastes, resort is made to bioassay where the effect of the waste on test organisms is determined.

The biological safety of a water means its freedom from pathogenic organisms, of which the common types are bacteria, viruses, protozoa, and multicelled parasites. In most instances pathogens enter the water by the fecal route. The direct determination of pathogens, especially viruses, is very difficult at present and impossible for effective control purposes. Resort is therefore made to indicator organisms, specifically the coliform group, present in the intestinal tracts of all warm-blooded animals. Their presence in a water is presumptive evidence of fecal contamination and hence the possible presence of pathogens (Ref. 5,7).

Table I show the standards in effect in 1968; substantial revisions are in progress, particularly in the chemical standards (Ref 5,8,9). The bacteriological standards will likely be expanded to include viruses when laboratory technique permits, especially with increasing water re-use. For the present, emphasis is on coliforms and the associated determination of residual disinfectant (chlorine, ozone). The increasing use of instrumentation in the biomedical field is only very slowly being reflected in water bacteriology, as the paucity of entries attests.

The current chemical standards are also displayed in Table 1. The chemical safety of water undergoes constant conceptual change as more is learned about the chemical nature of life. New toxicities are discovered (organic mercurials, selenium), new needs for trace elements are documented, and the proliferation of man-made chemicals seems to assure a dynamic future for chemical safety standards as applied to water.

C. WATER STANDARDS AND CRITERIA

In early history men were more concerned about the health-giving properties of water than in purifying those sources that were polluted. The first municipal water-filtration plant was built in Paisley, Scotland about 1800. By 1852 the city of London had passed an ordinance requiring that all water be filtered. Early water-quality standards included such parameters as color, odor, taste and turbidity. However, as later experience has shown, the quality of water can be adequately determined only by observing its chemical and physical properties and biological content. The U.S. Government expressed its interest in water pollution in the Harbors Act of 1899 and the Oil Pollution Act of 1924. Quoting from McKee and Wolf (Ref. 1): "The 1899 Act prohibits the depositing of waste materials, other than that flowing from streets and sewers in a liquid state, in or on the banks of navigable waters and their tributaries... The 1924 Act prohibits the discharge of oil into the coastal navigable waters of the United States."

"The third major federal enactment regarding water pollution was a provision in the Public Health Service Act of 1912, which gave specific authority to the Public Health Service to conduct investigations of the pollution of streams and lakes by sewage and other causes..."

"The first comprehensive-type legislation in the pollution control field was the Water Pollution Control Act of 1948...which authorized expanded activities by the Public Health Service .... This law...added the principles of State-Federal cooperative program development..."

Table 1.

Comparison of Various Drinking Water Standards (Ref. 5)

A. *Bacteriological Characteristics*

U.S. Public Health Service, 1962	AWWA Recommended Potable Quality Water Goals,[a] 1968
Water from the distribution system	Water from the distribution system
Dilution technique, five 10-ml portions	Dilution technique, five 10-ml portions
1. Not more than 10% of all portions examined each month shall show presence of coliform bacteria (coliform MPN ⋜ one per 100 ml) 2. No two consecutive samples taken from the same location, and not more than 5% of all samples examined each month, shall show presence of coliform bacteria in three or more of the five portions	No coliform organisms
Dilution technique, five 100-ml portions	Dilution technique, 100-ml portions
1. Not more than 60% of all portions examined each month shall show presence of coliform bacteria (coliform bacteria MPN ⋜0.9 per 100 ml) 2. No two consecutive samples taken from the same location, and not more than 20% of all samples examined each month shall show presence of coliform bacteria in all five portions examined	No coliform organisms
MF technique, using 50, 100, 200, or 500 ml	MF technique
1. The arithmetic mean coliform bacterial count of all samples examined during any month shall not exceed one per 100 ml 2. The coliform count per sample shall not exceed three per 50 ml, four per 100 ml, seven per 200 ml, or 13 per 500 ml in two consecutive samples taken from the same location, nor in more than 5% of all samples examined during any month	No coliform organisms

B. *Physical Characteristics*

Criterion	U.S. Public Health Service, 1962		AWWA Recommended Potable Quality Water Goals,[a] 1968
	Recommended limit[c]	Tolerance limit[c]	
Color, units	15	....	<3
Odor, threshold number	3, inoffensive	....	No odor
Residue:			
Filtrable, mg/l	500	....	<200
Nonfiltrable, mg/l	....	....	Virtually suspension-free
Total, mg/l	....	....	
Taste	Inoffensive	....	None objectionable
Turbidity, units	5	....	<0.1

C. *Chemical Constituents, mg/l*

Substance	U.S. Public Health Service, 1962		AWWA Recommended Potable Quality Water Goals,[a] 1968
	Recommended limit[c]	Tolerance limit[c]	
Alkyl benzene sulfonate (ABS)	0.5	....	<0.2
Aluminum (Al)	....	....	<0.05
Ammonia	....	....	
Arsenic (As)	0.01	0.05	
Barium (Ba)	....	1.0	
Cadmium (Cd)	....	0.01	
Calcium (Ca)	....	....	
Carbon alcohol extract (CAE)	....	....	<0.1
Carbon chloroform extract (CCE)	0.2	....	<0.04
Carbon dioxide, free (CO_2)	....	....	
Chloride (Cl)	250	....	
Chromium, hexavalent (Cr^{+6})	....	0.05	......
Copper (Cu)	1.0	....	<0.2
Cyanide (CN)	0.01	0.2	
Fluoride (F)	0.8–1.7[f,g]	1.4–2.4[f]	
Hardness (as $CaCO_3$)	....	....	80-100
Hydrogen ion concentration (pH)	....	....	
Iron (Fe)	0.3	....	<0.05
Lead (Pb)	....	0.05	
Magnesium (Mg)	....	....	
Magnesium + sodium sulfate	....	....	
Manganese (Mn)	0.05	....	<0.01
Nitrate (NO_3)	45	....	
Oxygen, dissolved (O_2)	....	....	
Phenolic compounds (as phenol)	0.001	....	
Selenium (Se)	....	0.01	
Silver (Ag)	....	0.05	
Sulfate (SO_4)	250	....	
Zinc (Zn)	5	....	<1.0

D. *Radioactivity, μμc/l*

Substance	U.S. Public Health Service 1962 Recommended limits[m]	AWWA Recommended Potable Quality Water Goals,[a] 1968
Radium 226 (Ra^{226})	3	
Strontium 90 (Sr^{90})	10	
Gross beta activity	1,000[n]	<100
Alpha emitters	.....	

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[a] Not a public health standard but desirable consumer goals.

[c] Recommended limit: (1) USPHS - Concentrations which should not be exceeded where more suitable water supplies are available. Tolerance limit: (1) USPHS - Concentrations above which shall constitute grounds for rejection of the supply.

[f] Dependent on annual average maximum daily air temperature over not less than a 5-yr period.

[g] Where fluoridation is practiced, minimum recommended limits are also specified.

[m] Water supplies containing concentrations in excess of these limits will be approved if surveillance of total intakes of radioactivity from all sources indicates that such intakes are within the limits recommended by the Federal Radiation Council for control action (see Chap. 13).

[n] In absence of strontium 90 and alpha emitters.

Finally, the particular concern of the Federal government in the growing national pollution problem resulted in the new Federal Water Pollution Control Act (P.L. 660, 84th Congress), which was approved by the President on July 9, 1956.

"The Federal Water Pollution Control Act amendments of 1961 considerably elevated the significance of the entire federal water-pollution-control program... It (was) now administered directly by the Secretary of the Department of Health, Education, and Welfare... The act states, in part, that the Secretary shall, 'in cooperation with other Federal, state, and local agencies have related responsibilities, collect and disseminate basic data on chemical, physical, and biological water quality insofar as such data or other information relate to water pollution and the prevention and control thereof'...." With this legislation the U.S. recognized that the primary responsibility for water pollution control rested with state governments.

The U.S. Public Health Service originally established Drinking Water Standards in 1914; these were revised repeatedly. In 1962 further revisions were made to "Standards to which drinking water and water supply systems used by (those) subject to Federal quarantine regulations must conform." (Ref. 8). The endorsement of these Standards by the American Water Works Association has resulted in general acceptance for all public supplies in the U.S. (Ref. 5).

In 1968 the American Water Works Association issued a report "Quality Goals for Potable Water", which defines "goals for non-toxic quality characteristics of the water delivered to the consumer." (Ref. 10). The bacteriological, chemical and physical recommendations and requirements for the two standards and goals listed above are reproduced from Ref. 5 and shown in Table 1.

Until 1970, drinking water standards of the U.S. Public Health Service and the World Health Organization did not include limits for mercury. In the spring of 1970, the U.S. Public Health Service tentatively proposed a standard of 5 ppb for mercury in drinking water (Ref. 11). Drinking Water Standards are presently under revision by EPA. Interim standards were issued March 14, 1975. See Appendix C.

The World Health Organization (WHO) issued revised European Standards for Drinking Water in 1970 (Ref. 12) and revised International Standards for Drinking Water in 1971 (Ref. 13).

The Federal Water Pollution Control Act (FWPCA) authorized both the states and the Federal Government to establish water quality standards for surface waters by 1967. Proposals submitted by the states and approved by the Department of the Interior become standards; if not approved, the Federal Government was empowered to set its own standards for the states. The water quality standards submitted by 50 states, 3 territories and the District of Columbia to the FWPC Administration in 1969 have been summarized in Ref. 14. The National Technical Advisory Committee on Water Quality Criteria studied the problem and developed criteria in the five general areas of water usage listed above. The far-reaching results of the study were published as Water Quality Criteria (Ref. 4). For public water supplies two types of criteria were considered: Permissible and Desirable Criteria. Permissible criteria listed the characteristics of raw surface waters which would allow the production of water which after treatment would meet the limits of the U.S. Public Health Service Drinking Water Standards. Desirable criteria listed the characteristics of raw surface water which would yield high quality treated water with either less treatment or a greater factor of safety. Table 2 (from Ref. 4) lists Surface Water Criteria for Public Water Supplies. The narrative notes for Table 2 are included in Appendix A.

Industrial water is used for cooling, cleaning and steam generation as well as a host of other processes. Although it may be thought that the requirement of industrial water are less severe than those of drinking water, paper and textile industries may require water with more stringent biological properties than drinking water! Even the best water will usually need further treatment for the production of pharmaceuticals.

Table 3 from Water Quality and Treatment, AWWA (Ref. 5) lists ranges in recommened limiting concentrations for industrial process waters.

The U.S. Geological Survey (USGS), as part of its water-data acquisition activities (Ref. 15), lists twenty-three water - quality parameters, the number of stations where each parameter is measured and the frequency of each measurement. Tables 4 and 5 from Ref. 15 list these statistics for surface water and ground water, respectively.

Ballinger (Ref. 16) summarizes current reporting requirements of industrial waste discharge:

TABLE 2.

Surface Water Criteria for Public Water Supplies (Ref. 4)

Constituent or characteristic	Permissible criteria	Desirable criteria	Paragraph
Physical:			
Color (color units)	75	<10	1
Odor	Narrative	Virtually absent	2
Temperature *	do	Narrative	3
Turbidity	do	Virtually absent	4
Microbiological:			
Coliform organisms	10,000/100 ml[1]	≤100/100 ml[1]	5
Fecal coliforms	2,000/100 ml[1]	<20/100 ml[1]	5
Inorganic chemicals:	(mg/l)	(mg/l)	
Alkalinity	Narrative	Narrative	6
Ammonia	0.5 (as N)	<0.01	7
Arsenic *	0.05	Absent	8
Barium *	1.0	do	8
Boron *	1.0	do	9
Cadmium *	0.01	do	8
Chloride *	250	<25	8
Chromium,* hexavalent	0.05	Absent	8
Copper *	1.0	Virtually absent	8
Dissolved oxygen	≥4 (monthly mean) ≥3 (individual sample)	Near saturation	10
Fluoride *	Narrative	Narrative	11
Hardness *	do	do	12
Iron (filterable)	0.3	Virtually absent	8
Lead *	0.05	Absent	8
Manganese * (filterable)	0.05	do	8
Nitrates plus nitrites *	10 (as N)	Virtually absent	13
pH (range)	6.0–8.5	Narrative	14
Phosphorus *	Narrative	do	15
Selenium *	0.01	Absent	8
Silver *	0.05	do	8
Sulfate *	250	<50	8
Total dissolved solids * (filterable residue).	500	<200	16
Uranyl ion *	5	Absent	17
Zinc *	5	Virtually absent	8
Organic chemicals:			
Carbon chloroform extract * (CCE)	0.15	<0.04	18
Cyanide *	0.20	Absent	8
Methylene blue active substances *	0.5	Virtually absent	19
Oil and grease *	Virtually absent	Absent	20
Pesticides:			
Aldrin *	0.017	do	21
Chlordane *	0.003	do	21
DDT *	0.042	do	21
Dieldrin *	0.017	do	21
Endrin *	0.001	do	21
Heptachlor *	0.018	do	21
Heptachlor epoxide *	0.018	do	21
Lindane *	0.056	do	21
Methoxychlor *	0.035	do	21
Organic phosphates plus carbamates.*	0.1[2]	do	21
Toxaphene *	0.005	do	8
Herbicides:			
2,4-D plus 2,4,5-T, plus 2,4,5-TP *	0.1	do	21
Phenols *	0.001	do	8
Radioactivity:	(pc/l)	(pc/l)	
Gross beta *	1,000	<100	8
Radium-226 *	3	<1	8
Strontium-90 *	10	<2	8

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[*] *The defined treatment process has little effect on this constituent.*

[1] *Microbiological limits are monthly arithmetic averages based upon an adequate number of samples. Total coliform limit may be relaxed if fecal coliform concentration does not exceed the specified limit.*

[2] *As parathion in cholinesterase inhibition. It may be necessary to resort to even lower concentrations for some compounds or mixtures. See par. 21.*

For Narrative notes see Appendix A.

TABLE 3.

Ranges in Recommended Limiting Concentrations for Industrial Process Waters

(Except as Noted, Units are mg/l) (Ref. 5)

Use	Turbidity, units	Color, units	Taste and odor threshold	Dissolved solids	Hardness, as $CaCO_3$	Alkalinity, as $CaCO_3$	pH, units	Chlorides, as Cl	Sulfates, as SO_4	Iron, as Fe	Manganese, as Mn	Iron plus manganese	Hydrogen sulfide	Fluorides, as Fl	Other requirements
Air conditioning	...	...	Low	...	...	...	...	...	...	0.5	0.5	0.5	...	...	Not corrosive or slime-promoting
Baking	10	10	None-low	...	[a]	...	...	...	...	0.2	0.2	0.2	0.2	...	Potable
Boiler feed							See Chap. 16								Potable if steam is used for food preparation
Brewing	0-10	0-10	None-low	500-1,500[b]	[c]	75-80[d]	6.5-7.0[e]	60-100	...	0.1	0.1	0.1	0.2	1.0	Potable; numerous other requirements
Carbonated beverages	1-2	5-10	None-low	850	200-250	50-130	...	250	250	0.1-0.2	0.2	0.1-0.4	0-0.2	0.2-1.0	Potable; COD, 1.5; organic matter, infinitesimal; algae and protozoa, none
Confectionery	...	...	Low	50-100	Soft	...	>7.0	...	...	0.2	0.2	0.2	0.2	...	Potable
Cooling							See Chap. 16								
Dairy	...	None	None	500[f]	180	...	...	30-	60	0.1-0.3	0.03-0.1	...	...	...	Potable; NO_3-N, 5.5; NO_2-N, 0; NH_3N, trace only; COD as $KMnO_4$, 12
Drinking	5	15	3, inoffensive	500	...	...	...	250	250	0.3	0.05	...	...	1.4-2.4[g]	Potable. See appendix to this chapter
Food canning and freezing	1-10	...	None-low	850	[h]	30-250	≥7.5	...	...	0.2	0.2	0.2-0.3	1.0	1.0	Potable; free from saprophytic organisms; NaCl, 1,000-1,500; NO_3-N, 2.8; NH_3-N, 0.4
Food equipment, washing	1	5-20	None	850	10	...	...	250	...	...	...	0.1	...	1.0	Potable; organic matter, infinitesimal
Food processing, general	1-10	5-10	Low	850	10-250	30-250	...	...	...	0.2	0.2	0.2-0.3	...	1.0[i]	Potable
Ice manufacture	5	5	Low	170-1,300	...	...	...	...	...	0.2	0.2	0.2	...		Potable; SiO_2, 10
Laundering	...	...	...	...	0-50	60	6.0-6.8[e]	...	...	0.2-1.0	0.2	0.2-1.0			
Paper and pulp, fine	10	5	...	200	100[j]	75	...	...	...	0.1	0.05	...	...	...	Soluble SiO_2, 20; free CO_2, 10; residual Cl_2, 2
Paper, groundwood	50[k]	30	...	500	200	150	...	75	...	0.3	0.1	...	...	...	Soluble SiO_2, 50; free CO_2, 10
Paper, kraft, bleached	40	25	...	300	100	75	...	200	...	0.2	0.1	...	...	...	Soluble SiO_2, 50; free CO_2, 10
Paper, kraft, unbleached	100	100	...	500	200	150	...	200	...	1.0	0.5	...	...	...	Soluble SiO_2, 100; free CO_2, 10
Paper, soda and sulfate pulps	25[k]	5	...	250	100[l]	75	...	75	...	0.1	0.05	...	...	...	Soluble SiO_2, 20; free CO_2, 10
Rayon and acetate fiber pulp production	5	5	...	100[f]	8	50-75	...	...	...	0.05	0.03	0.05	...	...	Al_2O_3, 8; Si, 25; Ca, 5
Rayon manufacture	0.3	...	...	...	55	...	7.8-8.3	...	...	0.0	0.0	0.0			
Sugar	...	...	...	Low	Low	...	...	20	20	0.1	...	...	...	...	Ca, 20; Mg, 10; bicarbonate, as $CaCO_3$, 100; sterile, no saprophytic organisms
Tanning	20	10-100	...	...	50-500	130	6.0-8.0	...	...	0.1-0.2	0.1-0.2	0.2	...	...	Bicarbonate hardness, low
Textile	0.3-25	0-70	...	...	0-50	...	...	100	100	0.1-1.0	0.05-1.0	0.2-1.0	...	...	COD, 8; heavy metals, none; Ca, 10; Mg, 5; bicarbonate, as $CaCO_3$, 200

[a] Some calcium is necessary for yeast action. Too much hardness retards fermentation, but too little softens the gluten to produce soggy bread. Water of zero hardness is required for some cakes and crackers.

[b] Not more than 300 mg/l of any one substance.

[c] $CaSO_4$ less than 100 to 500 mg/l; $MgSO_4$ less than 50 to 200 mg/l.

[d] For dark beer alkalinity as $CaCO_3$ may be 80 to 150 mg/l.

[e] Range, lower to upper limits.

[f] Total solids.

[g] Tolerance limit depends on annual average of maximum daily air temperatures for a minimum of 5 years.

[h] For legumes, 25 to 75; for fruits and vegetables, 100 to 200; for peas, 200 to 400.

[i] 1.5 mg/l of fluoride has been reported to cause embrittlement and cracking of ice.

[j] Calcium hardness, 50.

[k] No gritty material.

[l] Calcium hardness, 50; magnesium hardness, 50.

TABLE 4.

Parameter, Frequency of Measurement, and Number of Stations on Surface Waters Where Measurements Were Made (Ref. 15)

Parameter	Frequency									Total
	Continuous	Daily	Weekly	Monthly	Quarterly	Annual	Seasonal	Other periodic	Irregular	
	Number of stations									
Temperature	816	850	493	2,459	1,181	519	112	968	2	7,400
Specific conductance	241	419	111	2,002	770	757	111	822	2	5,235
Color	2	66	148	903	913	508	7	621	0	3,168
pH (field)	82	49	99	1,088	508	130	63	571	0	2,590
pH (laboratory)	5	512	268	1,749	1,070	769	120	927	1	5,421
Dissolved solids	9	212	173	1,562	1,007	799	93	863	2	4,720
Chloride	10	110	150	1,596	682	844	33	879	6	4,310
Nutrients--Nitrogen	1	27	213	1,369	821	536	67	759	0	3,793
--Phosphorus	6	27	179	1,038	956	564	49	866	0	3,685
Common ions	6	469	142	1,684	900	842	129	1,011	3	5,186
Hardness	4	387	176	1,571	957	808	93	669	1	4,666
Radiochemical	6	5	44	220	528	141	14	234	2	1,194
Dissolved oxygen	106	37	336	1,599	772	659	78	583	0	4,170
Minor elements	0	5	3	188	154	139	26	240	0	755
Pesticides	1	0	7	62	54	115	11	113	1	364
Detergents	0	3	85	353	528	25	31	125	0	1,150
Coliform	2	227	328	1,386	846	74	26	335	0	3,224
BOD	0	6	236	1,002	772	86	22	136	0	2,260
Carbon--Total	0	4	4	90	67	10	0	11	0	186
Other micro-organisms	2	10	110	263	195	34	20	117	0	751
Sediment--Suspended	20	282	72	244	78	42	2	365	7	1,112
Particle size--										
Suspended	5	17	4	130	82	46	13	365	7	669
Bed Material	0	0	0	51	8	13	1	110	0	183

TABLE 5.

Parameter, Frequency of Measurement, and Number of Stations on Ground Waters Where Measurements Were Made (Ref. 15)

Parameter	Frequency									Total
	Continuous	Daily	Weekly	Monthly	Quarterly	Annual	Seasonal	Other periodic	Irregular	
	Number of stations									
Temperature	33	30	20	89	275	1,236	46	1,709	1	3,439
Specific conductance	13	19	24	55	51	1,185	48	1,410	2	2,807
Color	6	7	35	129	34	794	2	886	0	1,893
pH (field)	8	31	23	113	11	671	7	931	0	1,795
pH (laboratory)	7	29	37	68	38	1,205	43	2,043	0	3,470
Dissolved solids	7	14	27	50	49	1,472	38	1,496	2	3,155
Chloride	7	15	30	111	119	558	40	1,852	2	2,734
Nutrients--Nitrogen	3	1	19	24	13	335	5	1,158	0	1,558
--Phosphorus	6	12	19	12	6	253	1	1,072	0	1,381
Common ions	20	20	9	95	273	1,660	43	2,020	3	4,143
Hardness	3	31	25	75	58	1,328	43	1,471	1	3,035
Radiochemical	3	3	10	118	263	126	0	96	0	619
Dissolved oxygen	3	1	19	16	2	78	0	65	2	186
Minor elements	0	0	1	4	3	70	0	99	14	191
Pesticides	0	0	2	0	0	17	0	3	10	32
Detergents	0	9	22	23	5	85	0	6	0	150
Coliform	6	18	124	843	116	532	0	544	0	2,183
BOD	0	1	6	26	0	1	0	1	0	35
Carbon--Total	0	0	12	2	0	0	0	0	0	14
Other micro-organisms	0	0	4	39	0	0	0	1	0	44
Sediment--Suspended	0	1	0	1	3	15	0	236	0	256
Particle size--Suspended	0	0	0	0	5	0	0	0	0	5

"The Refuse Act of 1899 requires a permit from the Environmental Protection Agency for all industrial waste discharges to navigable waters in the United States" (Ref. 17). "As a condition of the permit, the applicant must furnish data on 11 standard waste parameters [alkalinity, biochemical oxygen demand, chemical oxygen demand, total solids, total dissolved (filterable) solids, total suspended (nonfilterable) solids, total volatile solids, ammonia, kjeldahl nitrogen, nitrate, and total phosphorus] and a selected group of additional measurements depending on the type of industry." Table 6 shows the additional requirements for several Standard Industrial Classifications (SIC) as examples of the expanded list of waste parameters.

"The required tests are designed to characterize the volume and concentration of the major constituents. The measurements listed above, when applied to all industrial discharges, permit comparison between treated and untreated effluents and indicate the degree of "damage" to the receiving water in terms of oxygen depletion, sedimentation, pH change, and nutrient impact. The additional measurements required (Table 6) identify the waste contributions from specific industrial operations."

The standards and recommendations of the FWQA have continued when regulation of water standards was transferred to the EPA. A recently enunciated policy of EPA states, "Standards, the first nationwide strategy for water quality

TABLE 6.

Examples of Waste Parameters Sampled

SIC 26. Paper and allied products	
Color	Chromium
Specific conductance	Copper
Bromide	Lead
Chloride	Mercury
Sulfate	Nickel
Sulfite	Sodium
Phenols	Zinc
Total organic carbon	Total coliform

SIC 284. Soap, detergents, and cleaning preparations, perfumes, cosmetics, and other toilet preparations	
Color	Cyanide
Specific conductance	Sulfate
Turbidity	Sulfide
Oil and grease	Phenols
Chloride	Surfactants
	Total coliform

SIC 2871. Fertilizers	
Color	Cadmium
Turbidity	Chromium
Hardness	Copper
Oil and grease	Iron
Chloride	Lead
Fluoride	Manganese
Nitrite	Mercury
Pesticides	Nickel
Phosphorusortho	Zinc
Sulfate	Radioactivity
Aluminum	Total coliform
Arsenic	Fecal coliform

management, contain four major elements: the use (recreation, drinking water, fish and wildlife propagation, industrial, or agricultural) to be made of the interstate water; criteria to protect those uses; implementation plans (for needed industrial-municipal waste treatment improvements, among others) and enforcement plans; and an antidegredation statement to protect existing high quality waters" (Ref. 18).

EPA recently published effluent guidelines relating to toxic pollutants (e.g., Cd, Hg, cyanide, pesticides) and industry point source limitations for canned and preserved fruits and vegetables (e.g., BOD 5, pH) in the Federal Register. These sections are reproduced in Appendix B and Appendix C.

D. ORGANIZATIONS

The number of organizations interested in water quality is very large. The U.S. Geological Survey Digest of the Catalog of Information on Water Data (Ref. 15) lists 12 federal agencies and 159 non-federal agencies which report water-quality data.

Several organizations are listed below which are engaged in water-monitoring activities. Additional organizations are listed in Ref. 15.

The Federal Water Pollution Control Administration (FWPCA) was established in 1965 under the Department of Health, Education and Welfare to provide research and development grants, increased funds for construction of sewage treatment plants and to establish water quality criteria. The organization was transferred to the Department of the Interior in 1966; its name was changed to Federal Water Quality Administration in 1970 and later that same year its functions were transferred to EPA.

The Environmental Protection Agency (EPA) was established in 1970 "to assure the protection of the environment by abating and controlling pollution on a systematic basis". The EPA is responsible for water-quality control and management. The office of Water Programs, the Office of Enforcement and the Office of Research and Monitoring, all located at the Environmental Protection Agency, Washington D.C. 20460 are responsible for standards and guidelines. EPA laboratories conducting analysis and providing support include the following:

Arctic Environmental Research Laboratory
Environmental Protection Agency
Fairbanks, AK 99701

Analytical Quality Control Laboratory
1014 Broadway
Cincinnati, OH 45260

Gulf Breeze Environmental Research Laboratory
P.O. Box 158
Dauphin Island, AL 36528

National Environmental Research Center
Las Vegas, NV 89114

National Environmental Research Center
Cincinnati, OH 45260

National Environmental Research Center
200 S.W. 35th St.
Corvallis, OR 97330

National Marine Water Quality Laboratory
P.O. Box 277
West Kingston, RI 02892

National Marine Water Quality Laboratory
Bears Bluff Field Site
Box 368
Johns Island, SC 29455

Robert S. Kerr Water Environmental
Research Laboratory
P.O. Box 1198
Ada, OK 74820

Southeast Environmental Research Laboratory
College Station Rd.
Athens, GA 30601

The U.S. Public Health Service (USPHS) was founded in 1798; it is the "federal agency specifically charged with promoting and assuring the highest level of health attainable...". The three operating agencies of USPHS are the Food and Drug Administration, the Health Service and Mental Health Administraiton and National Institutes of Health, all with headquarters in Washington, D.C.

The U.S. Geological Survey (USGS) was established as an agency in the Department of the Interior in 1879. Its activities include the Water Resources Division which is responsible for the appraisal of the quantity and quality of our national water resources and research in the field of hydrology. The USGS shares with state and local water agencies in investigations on both surface and ground water - development conservation and management. Water-quality data are processed through the computerized data file in Washington. The first of the Water Resources Division's Centeral Laboratories is located in Salt Lake City, UT. Fourteen other water-quality laboratories are located throughout the country. For information contact:

U.S. Geological Survey
18th & F Streets, N.W.
Washington, DC 20240

The National Oceanic and Atmospheric Administration (NOAA), among other activities, conducts research related to the oceans and inland waters. It also provides satellite observations of the environment. Address:

National Oceanic and Atmospheric
Administration
6010 Executive Blvd.
Rockville, MD 20852
(301) 656-4060

The Bureau of Reclamation is involved in the regulation, conservation and utilization of water and related land resources in the western states. Address:

Bureau of Reclamation
Department of the Interior
Washington, DC 20240
(202) 343-4662

The American Public Health Association (APHA) promotes personal and public health by, among other things, establishing standards, procedures and tabulating facts on the causes of communicable diseases. Address:

American Public Health Association
1015 - 18th St., N.W.
Washington, DC 20036
(202) 833-9640

American Water Works Association (AWWA) has interests in water supplies, water departments and associated equipment. AWWA issues a monthly journal covering the various aspects of water. Address:

American Water Works Association
2 Park Avenue
New York, NY 10016
(212) 686-2040

The Water Pollution Control Federation (WPCF) is a federation of 50 technical societies. Membership includes chemists and engineers concerned with the collection, treatment and disposal of wastewaters. WPCF published a monthly journal. Address:

Water Pollution Control Federation
3900 Wisconsin Ave., N.W.
Washington, DC 20016
(202) 362-4100

The main concerns of the American Society for Testing and Materials are performance standards and test methods for materials and the products made from these materials. Part 23 of the Annual Book of ASTM Standards (Ref. 3) is relevant to water and water analysis. The 1972 edition of this volume includes over 150 standards for water and atmospheric analysis. Standards comprise test methods, definitions, recommended practices, classifications and specifications that have been formally adopted by the Society. New editions of Part 23 are published each November. Among the many technical committees is ASTM Committee D-19 on Water. A Journal of Materials is published quarterly. ASTM may be contacted at:

American Society for Testing and Materials
1916 Race Street
Philadelphia, PA 19103
(215) 569-4200

Battelle Memorial Institute began operations in 1929. It is a non-profit organization with five major research centers engaged in pure and applied research. Among its activities is an interest in many aspects of water quality. Headquarters address:

Battelle Memorial Institute
505 King Avenue
Columbus, OH 43201
(614) 299-3151

E. INFORMATION SOURCES

1. Catalogs

The U.S. Geological Survey publishes an annual Catalog of Information on Water Data, which reports on water-data acquisition activities on streams, lakes, reservoirs, estuaries and ground water. A helpful digest of the catalog information is available (Ref. 15). In the 1970 edition of the Catalog water-quality activities of both Federal and non-federal agencies are reported. Information on water data is listed in one of four indexes: Index to Water-Quality Section, Index to Surface-Water Section (with 23,846 stations reporting), Index to Ground-Water Stations (with 28,964 stations reporting) and Index to Areal Investigations and Miscellaneous Activities.

The Catalog information is accessible through data-retrieval methods; however, the actual water data must be obtained from the reporting agencies.

2. Abstracts

The Water Resources Information Center (WRIC) is responsible for publishing Selected Water Resources Abstracts (SWRA). Abstracts appear twice a month of journal articles and reports on the water-related aspects of science and engineering. An annual index is published in two parts: Part 1 is arranged by Author, Organization and Accession Number; Part 2, by Subject. Federal agencies, contractors and grantees in water resources may request the SWRA from the Manager:

Water Resources Scientific Information
Center
Office of Water Resources Research
U.S. Department of Interior
Washington, DC 20240

SWRA is also available on subscription from the

National Technical Information Service
U.S. Department of Commerce
Springfield, VA 22151

The Environmental Awareness Reading List (EARL) is a semi-monthly listing of current publications dealing with environmental concerns compiled by the Natural Resources Library of the U.S. Department of the Interior. These selections are intended to reflect current developments and discussions concerning environmental and natural resource topics appearing in a variety of both popular and technical periodicals. The entries include full bibliographic citations--annotations are added when needed to clarify a title. The arrangement is alphabetical by author or title.

The Environmental Awareness Reading List is a cooperative product of the National Park Service and the Natural Resources Library. Yearly subscriptions are available through:

National Technical Information Service
U.S. Department of Commerce
Springfield, VA 22151

Environmental Information Access is published semi-monthly by:

Environment Information Center, Inc.
124 E. 39th Street
New York, NY 10016

Water Pollution Abstracts cover international literature on water and water collection; the Abstracts are published monthly by:

The Department of the Environment
Her Majesty's Stationery Office
London, England

3. Data Bases

Information on water monitoring is being gathered and stored in a number of data bases. A data base may be defined as a collection of information in machine-readable form. Database information may be in the form of documents or data. In document form, an abstract or perhaps the entire document is available for re-call. In data form the original data with perhaps some consolidation are available for readout. Several data bases are noted here:

STORET In 1961 the staff of the National Water Quality Network in the Division of Water Supply and Pollution Control, U.S. Public Health Service conceived the basic concept for the storage and retrieval of data for water pollution control. In 1966 the STORET System was transferred into the Federal Water Pollution Control Administration; a refinement of the system is now operated by the Division of Applied Technology, EPA. This Water Quality Control Information System is set up to store and retrieve data and information on such topics as water quality, standards, municipal and waste discharges and waste abatement needs. In the U.S. there are now more than 150 terminals with access to STORET. A description on how to use the system is given in the STORET Handbook available from the Water Quality Control Information System (STORET), EPA, Washington, DC 20460.

Water Resources Abstracts is a document form of data base. For information on retrieval, contact:

Water Resources Information Center
University of Oklahoma
Norman, OK 73069

The National Environmental Research Center maintains a computer-accessed literature file on analytical methods for determining water quality. Also available is a monthly abstract bulletin. Address:

Analytical Quality Control Laboratory
National Environmental Research Center, EPA
1014 Broadway
Cincinnati, OH 45260

The Analytical Methodology Information Center (AMIC) is being created for EPA's Analytical Quality Control Laboratory by the Columbus Ohio Laboratories of Battelle Institute. The center plans to gather, analyze, and disseminate technical information on methods for determining water quality and effects of pollutants. Address:

Battelle Columbus Laboratories
505 King Avenue
Columbus, OH 43201

F. METHODS OF ANALYSIS

1. Origin of Standards

Methods for the analysis of water quality parameters have progressed significantly during the past one hundred years. The first edition of Standard Methods of Water Analysis appeared in 1905. Since then twelve editions have appeared at about 5 year intervals each with refinements and improvements so that the 13th Edition of Standard Methods for the Examination of Water and Wastewater (1971) was immediately accepted as a standard reference work for water analysis in the U.S. The 13th edition is the joint work of the American Public Health Association, the American Water Works Association and the Water Pollution Control Federation. Quoting from the preface, "The methods presented ...are the best available and generally accepted precedures for the analysis of water and wastewaters...

"All methods...are 'standard' unless designated 'tentative'... Methods with 'standard' status have been extensively studied and accepted as applicable within the limits of sensitivity, precision and accuracy recorded. 'Tentative' methods are those still under investigation which have not yet been fully evaluated or are not considered sufficiently specific at present to be designated 'standard'...".

In the interim between editions,a new method may be adopted as tentative or standard by the Joint Editorial Board. Details of such action will be published in the journal of one of the three sponsoring agencies and an announcement made in the journals of the other two. The advantage of the above procedure is that each technique has been repeated a great many times and its operation quite well understood before consideration as a standard. A disadvantage is that a great deal of elapsed time takes place before a really new technique is accepted on a wide-spread basis.

The ASTM Standards Part 23, Water; Atmospheric Analysis (1972) includes water sampling and analytical methods, corrosivity tests and methods of reporting. These standards, which are revised annually, represent a background of wide technical experience and analytical ability. The standards are used extensively in the examination of industrial waters and waste waters.

The EPA has much concern for the analytical procedures for measuring water quality. Methods for Chemical Analysis of Water and Waste 1971 (Ref. 19) lists several criteria for choosing the analytical procedures to be followed by the EPA Water Quality Office (WQO) laboratories:

"(1) The method should measure the desired constituent with precision and accuracy sufficient to meet the data needs of WQO in the presence of the interferences normally encountered in polluted waters."

"(2) The procedures should utilize the equipment and skills normally available in the typical water pollution control laboratory."

"(3) The selected methods are in use in many laboratories or have been sufficiently tested to establish their validity."

"(4) The methods should be sufficiently rapid to permit routine use for the examination of a large number of samples."

EPA is to be commended for its emphasis that "instrumental methods have been selected in preference to normal procedures because of the improved speed, precision and accuracy."

EPA recently published guidelines establishing test procedures for the analysis of pollutants in water. These guidelines require that discharge measurements, including but not limited to the pollutants and parameters listed in Table I, Appendix D, be performed by the test procedures indicated; or under certain circumstances by other procedures. See Appendix D.

The U.S. Geological Survey has prepared a series of manuals on techniques for water-quality investigations. The material is divided into subject headings called books and subdivided into sections and chapters. Section A of Book 5 deals with water analysis. Chapter 1 is entitled, "Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases," (Ref. 20). The manual contains methods used by the Survey to collect, preserve, and analyze water samples for their content of dissolved minerals and gases. Also discussed are laboratory equipment and instrumental techniques, accuracy and precision of analysis, and reporting of results. Seventy-six analytical procedures are given for determining 55 water properties. The instrumental methods include atomic absorption for 19 metals and the ion-specific electrode method for fluoride. Chapter 3 is "Methods for Analysis of Organic Substances in Water." (Ref. 21).

In summary, current knowledge about pollutants and their sources ranges from comprehensive reports on many of the pollutants to sparse or nonexistent information on other potential ones. Likewise, analysis techniques are well established for many of the pollutants; yet for several others the techniques are still in various stages of development, and commercially available instruments do not exist. In addition to the References mentioned above, References 1, 4, 5, 8, 9, 22, 23, 24, and 25 offer very useful information on water analysis and techniques.

2. Water-Monitoring Instrumentation

The use of water-monitoring instrumentation is increasing and in many areas it is replacing manual analytical techniques. The shift toward automated methods results from 1) the need to record data continuously, 2) the availability of data processing equipment to provide more rapid analysis of samples, 3) the accuracy provided by well-calibrated equipment, 4) the ease of determining results from well-designed instrumentation and 5) the potential for lower manpower requirements. Instruments are usually designed with field or laboratory service in mind; both types of equipment are included in this Survey and are treated separately.

When designing a system for a specific monitoring problem, several factors must be considered. At the core of such a system is an instrument or technique for analysis of the constituent of concern. Constituents and the instrumental techniques used for their detection are listed in Table 7. This list places emphasis on instruments and analyzers and does not attempt to list all of the several hundred manual methods of analysis. The number of analytical techniques is certainly not complete; however, the table should give an indication of the complexity and magnitude of the monitoring problem. It must be emphasized that the analytical instrument or technique alone does not complete the monitoring system.

Systems used for measuring water parameters can be thought of as including the following steps (but not necessarily always in this order):

1. Sampling
2. Sample preservation
3. Sample pre-analysis treatment including pollutant separation and/or concentration and pre-measurement chemical reaction(s)
4. Pollutant or parameter measurement
5. Data acquisition and reduction

Instrumental methods for performing steps 1, 2 and 3 will be treated in a separate section. They are also discussed individually where they affect the performance of that instrument. Instrumentation discussed in this Survey is divided into three classes according to the steps required for final measurement: (a) Continuous-Sensor-type instruments which follow steps 4 and 5 (b) Batch-Sampling type instruments which follow the sequence 1, 3, 4 and 5, and (c) Laboratory Analysis Instrumentation which follows the entire sequence 1 through 5.

a. Continuous-Sensor Type Instruments measure a constituent or parameter on an uninterrupted basis. Instruments in this class may be further subdivided into 1) those which do not require pretreatment of the pollutant (e.g. the addition of reagents), and 2) those normally employing pretreatment, such as added pH buffers and decomplexing agents for ion-specific electrodes. Water-quality parameters of the first category measured include pH, temperature, turbidity, conductivity, and dissolved oxygen and residual chlorine. Sensors in the second category utilize ion-selective electrodes for monitoring of some anions.

b. Batch-Sampling Type Instruments measure a constituent or parameter on an interrupted or sampled basis; the analysis is then performed on this discrete sample. Instruments in this class may be further subdivided into 1) those which are operated manually and 2) automated monitors. A number of systems with multiparameter capabilities fall into this category. These include monitors for such diverse pollutants as Cu, cyanide, Cr, phenol and residual chlorine and parameters including pH, and conductivity. Systems are also available for measuring one pollutant at a time.

c. Laboratory Analysis Instrumentation ordinarily operates in the laboratory due to the constraints of operator intervention, operational environment, fragility or high maintenance requirements. Instruments in this category include Gas Chromatographs/Mass Spectrometers, Atomic Absorption Spectrometers, X-Ray Fluorescence Analyzers, Emission Spectrometers and Neutron-Activation Analyzers.

Of primary concern are the reliability, durability, and ruggedness of a complete monitoring system. These nebulous qualities, which are more desirable than extremely high accuracy and other quantitative characteristics, determine the required degree of inspection, maintenance, and repair. This is especially important in on-site monitoring in which the operating conditions may be quite hostile. Depending upon the desired frequency of data, available manpower, and accessibility, one might also appreciate the capability of unattended operation for extended periods.

Versatility of the system is of concern if several pollutants are to be monitored. Multiparameter capability of major portions of a system can save considerable expenditure.

TABLE 7.

Instrumental Techniques for Water Monitoring

METALS (all forms)

All Metals Listed Herein:	Atomic Absorption Spectrophotometry Emission Spectrometry Molecular Absorption Spectrophotometry (except Ca, Na, Ti)
Aluminum:	Spark Source Mass Spectrometry
Beryllium:	
Boron:	Direct Reading Emission Spectrometry Potentiometric
Cadmium:	Atomic Fluorescence Electrochemical
Calcium:	Atomic (Flame) Emission Spark Source Mass Spectrometry X-Ray Fluorescence
Chromium:	Chemiluminescence Electrochemical Spark Source Mass Spectrometry X-Ray Fluorescence
Copper:	Atomic Fluorescence Electrochemical Spark Source Mass Spectrometry X-Ray Fluorescence
Iron:	Atomic Fluorescence Chemiluminescence Spark Source Mass Spectrometry
Lead:	Electrochemical Spark Source Mass Spectrometry X-Ray Fluorescence
Magnesium:	Spark Source Mass Spectrometry
Manganese:	Direct Reading Emmission Spectrometry Spark Source Mass Spectrometry
Mercury:	Atomic Fluorescence Neutron Activation X-Ray Fluorescence
Nickel:	Polarographic Spark Source Mass Spectrometry X-Ray Fluorescence
Potassium:	Atomic (Flame) Emission Ion Selective Electrode Spark Source Mass Spectrometry X-Ray Fluorescence

METALS (Continued)

Selenium:	Molecular Fluorescence
Silicon:	
Silver:	X-Ray Fluorescence
Sodium:	Atomic (Flame) Emission Ion Selective Electrode Spark Source Mass Spectrometry
Strontium:	Atomic (Flame) Emission
Titanium:	Spark Source Mass Spectrometry X-Ray Fluorescence
Vanadium:	Neutron Activation Spark Source Mass Spectrometry
Zinc:	Atomic Fluorescence Electrochemical Spark Source Mass Spectrometry X-Ray Fluorescence

HALIDES AND CYANIDE

Fluoride:	Ion Selective Electrode Molecular Absorption (Colorimetric)
Chloride:	Ion Selective Electrode Molecular Absorption (Colorimetric) Potentiometric (Ag-AgCl Electrode)
Bromide:	Molecular Absorption (Colorimetric)
Iodide:	Ion Selective Electrode Molecular Absorption (Colorimetric)
Cyanide:	Ion Selective Electrode Molecular Absorption (Colorimetric)

NITROGEN, PHOSPHORUS, SULFUR

Ammonia:	Activation Analysis Automated Colorimetric Colorimetric Ion Selective Electrode

TABLE 7. (Continued)

NITROGEN, PHOSPHORUS, SULFUR (Continued)

Nitrate:	Activation Analysis Automated Colorimetric Colorimetric UV Absorption
Nitrite:	Activation Analysis Automated Colorimetric Colorimetric Ion Selective Electrode
Organic Nitrogen:	Activation Analysis Automated Colorimetric Colorimetric
Total Nitrogen:	Activation Analysis Automated Colorimetric Colorimetric
Phosphate:	Automated Colorimetric Colorimetric (All Phosphorus) Continuous Colorimetric (Phosphate)
Sulfate:	Automated Colorimetric Turbidimetric
Sulfide:	Colorimetric Ion Selective Electrode
Sulfite:	Colorimetric

PHYSICAL AND CHEMICAL PARAMETERS

Conductivity:	Conductance Bridge
Hardness:	Automated Colorimetric Ion Selective Electrode
Salinity:	Conductance
pH:	Electrochemical
Alkalinity:	Automated Colorimetric Colorimetric Electrochemical
Acidity:	Colorimetric
Temperature:	Thermometer Thermistor Thermocouple
Turbidity:	Nephelometer Turbidimeter

BIOLOGICAL PARAMETERS

Biochemical Oxygen Demand (BOD):	DO Probe Respirometry/Manometric
Chemical Oxygen Demand (COD):	Colorimetric
Dissolved Oxygen (DO):	Membrane Probe
Total Organic Carbon:	Combustion Analyzer
Bacteria and Viruses:	Colony Counters Fluorescent Antibody Technique

DISSOLVED GASES

Chlorine:	Colorimetric Electrochemical
Hydrogen Sulfide:	Colorimetric Iodometric

PESTICIDES: INSECTICIDES, HERBICIDES, FUNGICIDES, TRACE TOXIC COMPOUNDS

Chlorinated Hydrocarbons:	Gas Chromatography Gas Chromatography/Mass Spectrometry/Computer

PHENOLICS	Gas Chromatography Thin-Layer Chromatography (Fluorescence) UV Spectrophotometry
PETROCHEMICALS	Gas Chromatography Gas Chromatography/Mass Spectrometry/Computer Thin-Layer Chromatography
OIL AND GREASE	Atomic Absorption Spectrophotometry Gas Chromatography IR Spectrophotometry Reflectance Sensors Thin-Layer Chromatography UV Spectrophotometry

d. Automated Instruments - Instruments that operate automatically exhibit several advantages over manually operated instrumentation: There is less likelihood of random error in performing the analysis; large volumes of data are handled more efficiently, one obtains faster turnaround time in data reduction; and operating personnel may be released for other tasks. The disadvantages of automated instruments are that they are more time consuming to set up initially (the effort is usually not worthwhile unless at least 50 samples are analyzed in the same time span), the equipment is more complicated to maintain and the initial cost is considerably greater. At present, trade-offs favor automated instrumentation when a multiplicity of measurements of the same nature are to be performed, e.g. a number of batch samples analyzed as rapidly as possible or a single water-quality parameter must be measured continually.

Proper calibration of instrumentation systems is important; unreliable data are worse than no data at all. This is of special importance if real-time information is used in the decision making process, for example, immediate corrective action for downstream receiving waters.

Some automatic environmental monitoring systems are capable of collecting data in computer compatible format. Data are recorded continuously at the monitoring site on punched paper tape or reusable magnetic tape. After an appropriate recording period tapes are transported to the computer center for analysis. An example is a Westinghouse system which can record water parameters such as flow, level, temperature, pH, DO and conductivity.

The use of an on-line computer to control data-acquisition activities is in its infancy in water monitoring. With the decreased cost of mini-computers and the availability of commercially available equipment to interface water monitors to computers, significant progress can be expected in the near future.

Users of this Survey are invited to comment on and criticize its contents. These comments will hopfully help insure the accuracy and completeness of the Survey. Such information should be communicated to the Environmental Instrumentation Group, Lawrence Berkeley Laboratory, Berkeley, CA 94720.

Units

m = meter
cm = centimeter
μm = micrometer
nm = nanometer
l = liter
ml = milliliter

μl = microliter
g = gram
mg = milligram
μg = microgram
ng = nanogram
pg = picogram
ppb = parts per billion
ppm = parts per million

M, molar solution = 1 gram molecular weight per liter (moles per liter)
N, normal solution = 1 gram equivalent weight per liter
m, molal solution = 1 gram molecular weight per 1000 g of water

Conversion Units (assuming one liter of water weighs one kg)

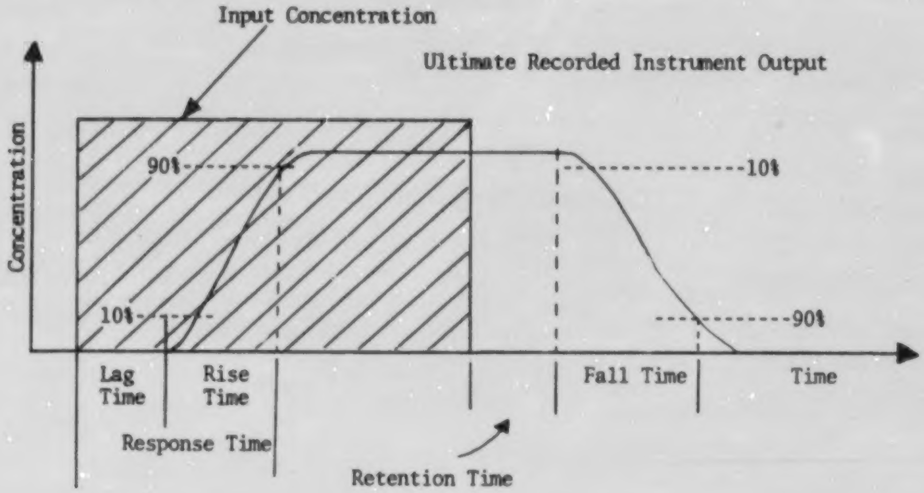
ppm = mg/l
ppb = μg/l
mg/l = μg/ml
ppm = 1000 ppb
g = 1000 mg
mg = 1000 μg
μg = 1000 ng
ng = 1000 pg
m = 10^9 nm

H. GLOSSARY

1. Terms Related to Instrument Notes

Class	Continuous-Sensor Type Instruments measure a constituent or parameter on an uninterrupted basis. These instruments may be used in the field or laboratory. Batch-Sampling Type Instruments measure a constituent or parameter on an interrupted or discrete sampled basis; the analysis is then performed on this sample. These instruments are usually used in the laboratory, but may be used in the field. Laboratory Analysis Instrumentation ordinarily operates in the laboratory due to the constraints of operator intervention, operational environment, fragility or high maintenance requirements.
Type of Use	Field operation usually denotes the use of portable equipment capable of analysis under a wide range of environmental conditions. Laboratory operation usually denotes use of fixed equipment capable of analysis only under restricted environmental conditions, this may include mobile laboratories used in the field.
Minimum Detectable Sensitivity	(Detection Limit) Concentration that produces a reading equal to twice the standard deviation of a series of measurements near the blank level.
Range	The minimum and maximum measurement limits (the minimum limit is usually reported as 0 μg/l; this is somewhat misleading, and it would be better to report it as the true minimum measurement limit).
Interferences	Any substance or species which causes a deviation of instrument output from the value which would result from the presence of only the desired constituent under test. Appreciable interferences are those greater than 10%. Moderate interferences are those between 5% and 10%. Slight or no interferences are those less than 5%. Where the interference percent is: $\frac{(X) - (C)}{(I)} \times 100 = \%$ interference and (X) = total response due to constituent and interference (C) = response due to constituent under test (I) = concentration of interference The unit of response or concentration must be common to all parameters and should be indicated.
Multiparameter Capability	Ability to measure other constituents or parameters
Sampling	Specified either as continuous or batch
Accuracy	The correctness in comparison to an independent or reference method. Generally calibration of the instrument involves adjustment of the instrument output to the value determined by the independent or reference method.
Reproducibility	The precision of the measurements - the degree of agreement between repeated measurements of the same concentration.
Linearity	The maximum deviation between an actual instrument reading and the reading predicted by drawing a straight line between the upper and lower calibration points.

Noise	Spontaneous deviation from a mean output not caused by input concentration changes.
Lag Time	The time interval from a step change in the input concentration at the instrument inlet to the first corresponding change in the instrument output.
Rise Time	The time interval between the initial reponse and a 90% response (unless otherwise specified) after a step increase in the inlet concentration.
Retention Time	The time interval from a step decrease in the input concentration at the instrument inlet to the first corresponding change in the instrument output.
Response Time	The time interval from a step change in the input concentration at the instrument inlet to a reading of 90% (unless otherwise specified) of the ultimate recorded output. This measurement is the same as the sum of lag time and rise time.
Fall Time	The time interval between the initial response and a 90% response (unless otherwise specified) after a step decrease in the inlet concentration. This measurement is usually, but not necessarily, the same as the rise time.



Zero Drift	The change with time in instrument output over a stated time period of unadjusted continuous operation when the input concentration is zero.
Span Drift	The change with time in instrument output over a stated time period of unadjusted continuous operation when the input concentration is a stated value other than zero.
References	Published or unpublished information pertaining to instrument specifications and performance characteristisc.
Categories of Water	Applicability of the instrumentation to the analysis of a pollutant or parameter in Fresh, Waste, and/or Saline water samples.

2. Terms Related to Water Monitoring

The following are some terms related to water monitoring. Definitions have been altered in some cases from those found in the references.

Absent	The most sensitive analytical procedure in Standard Methods for the Examination of Water and Wastewater, 13th edition (or other approved procedure), does not show the presence of the subject constituent.
Acclimated	Adapted to environmental change.
Acclimated Organism(s)	Seed organism(s) especially grown to cope with bio-oxidation-resistant organic wastes.
Acidity	The quantitative capacity of aqueous solutions to react with hydroxyl ions. It is measured by titration with a standard solution of a base to a specified end point. Usually expressed as milligrams per liter of calcium carbonate; that is, the amount of calcium carbonate that would be required to exactly neutralize the sample. (Ref. 26)
Activated-Carbon Filter	A filter used to remove dissolved organic matter from water for taste and odor control. Dissolved gases, liquids and finely divided solids may also be removed.
Activated Sludge	A gelatinous matrix imbedded with filamentous and unicellular bacteria which serve as food for protozoa. The bacterial genera which predominate depend on the characteristics of the wastewater being treated. The activated sludge treatment of wastewater purification is one of the most common secondary waste treatment processes.
Aeration	The bringing about of intimate contact between air and water by methods including: (a) spraying water into the air over a collecting basin or, (b) causing water to flow over baffles. (Ref. 4)
Aerobic	In the presence of air (or oxygen); an aerobic organism requires oxygen for respiration.
Aerobic Bacteria	Bacteria that require free elemental oxygen for their growth. Their metabolic demands can severely deplete the dissolved oxygen. (Ref. 4)
Aerobic Organotrophy	Organism which utilizes organic materials under aerobic conditions for its growth.
Aerobic Oxidation	Decomposition of organic matter by aerobic organisms.
Algae	Simple plants, many microscopic, containing chlorophyll. Freshwater algae are diverse in shape, color, size, and habitat. They are the basic link in the conversion of inorganic constituents in water into organic constituents. (Ref. 4)
Algicide	A specific chemical highly toxic to algae. Algicides are often applied to water to control nuisance algal blooms.
Alkalinity	The capacity of water to neutralize acids, a property imparted by the water's content of carbonates, bicarbonates, hydroxides, and occasionally borates, silicates and phosphates. It is expressed in milligrams per liter of equivalent calcium carbonate. (Ref. 26)
Anabolic	Relating to the growth portion of the metabolic process; e.g., new cell formation
Anaerobic Bacteria	Bacteria that grow only in the absence of free elemental oxygen. (Ref. 26)
Anaerobic Organism	An organism that thrives in the absence of oxygen.

Anaerobic Stabilization	Decomposition of waste by an anaerobic microbic population in the continuous absence of oxygen.
Aquatic Biota	Animal and plant life, or fauna and flora, of a stream or other water. (Ref. 26)
Assimilation Capacity	The extent to which a body of water can receive wastes without significant deterioration of beneficial uses. Suitability for a given use is defined in terms of quality criteria, and these are still to some extent arbitrarily designated. The criterion most widely used is dissolved oxygen, although that parameter is by no means always relevant.
ATP (Adenosine Triphosphate)	A high energy biochemical intermediary in enzyme catalyzed processes.
Auto-Oxidation	A self-induced or internally catalyzed oxidation process.
Autotrophic Organism	An organism capable of constructing organic matter from inorganic substances. (Ref. 4)
Bacteria	A group of universally distributed, rigid, essentially unicellular microscopic organisms lacking chlorophyll. Bacteria usually appear as spheroid, rod-like, or curved entities, but occasionally appear as sheets, chains, or branched filaments. Bacteria are usually regarded as plants. Some bacteria are the primary nuisance-type growths in rivers, lakes, and ponds, where the growths they produce can clog fishing nets and create unsightly conditions. (See aerobic bacteria; anaerobic bacteria.) (Ref. 4 and 26)
Bacteriocide	A substance which kills bacteria.
Bacteriostat	A substance which inactivates bacteria.
Benthic Region	The bottom of a body of water. This region supports the benthos, a type of life that not only lives upon but contributes to the character of the bottom. (Ref. 4 and 26).
Benthos	Aquatic bottom-dwelling organisms. These include: (1) sessile animals, such as the sponges, barnacles, mussels, oysters, some of the worms, and many attached algae; (2) creeping forms, such as insects, snails, and certain clams; and (3) burrowing forms, which include most clams and worms.
Bioassay	(1) An assay method using a change in biological activity as a qualitative or quantitative means of analyzing a material's response to biological treatment. (2) A method of determining toxic effects of industrial wastes and other wastewaters by using viable organisms as test organisms. (Ref. 26)
Biochemical Oxygen Demand (BOD)	"The quantity of oxygen required, expressed in mg/ , for the biological and chemical oxidation of water-borne substances under conditions of test." (Ref. 3, 4, BOD) BOD represents oxygen utilized in energy reactions which support synthesis of organic material into new cell material. For a given organic substance BOD is the summation of oxygen utilization in energy reactions. (Ref. 42, BOD)
Biological Stabilization	Occurs when the initially available substrate has been utilized by the bacteria in a bio-system to produce relatively stable, oxidation-resistant cellular end products. At this point the BOD curve approaches zero slope (in the absence of nitrification).
Biologically Available	Utilizable as a nutrient by the biota in the environment.
Biomass	The weight of all life in a specified unit of environment or an expression of the total mass or weight of a given population, both plant and animal.
Biostat	A substance which inhibits the biological activity (growth) of bacteria.
Biota	All living organisms of a region. (Ref. 4)

Bloom	Large, readily visible masses of microscopic and macroscopic plant life, such as green algae, occurring in bodies of water. (Ref. 26)
BOD	See Biochemical Oxygen Demand.
BCD Exertion	Oxygen requirement of a bio-system; biochemical oxygen demand equivalent.
Brackish	Saline, unpalatable.
Brackish Water	Water having a mineral content in the general range between fresh water and seawater. Water containing from 1,000 to 10,000 mg/l of dissolved solids. (Ref. 26)
Carbonaceous Oxygen Demand (Carbonaceous OD)	Oxygen demand exerted by organic carbon compounds present; oxygen required to convert organic carbon to CO_2.
Carbonate Hardness	Hardness caused by the presence of carbonates and bicarbonates of calcium and magnesium in water. Such hardness may be removed to the limit of solubility by boiling the water. When the hardness in numerically greater than the sum of the carbonate alkalinity and the bicarbonate alkalinity, that amount of hardness which is equivalent to the total alkalinity is called carbonate hardness. See hardness. (Ref. 26)
Cell Stabilization	See Biological Stabilization.
Chemical Oxygen Demand (COD)	A measure of the oxygen-consuming capacity of inorganic and organic matter present in water or wastewater. It is expressed as the amount of oxygen consumed from a chemical oxidant in a specific test. It does not differentiate between stable and unstable organic matter and thus does not necessarily correlate with biochemical oxygen demand. Also known as OC and DOC, oxygen consumed and dichromate oxygen consumed, respectively. (Ref. 26)
Chlorine Demand	The difference between the amount of chlorine added to water or wastewater and the amount of residual chlorine remaining at the end of a specified contact period. (REf. 26)
Chromogen	A reagent which produces a colored product.
Coenzyme	The non-protein moitié of an enzyme sys[illegible]m.
Cold-Blooded Animals (Poikilothermic Animals)	Animals that lack a temperature regulating mechanism that offsets external temperature changes. Their temperature fluctuates to a large degree with that of their environment. Examples are fish, shellfish, and aquatic insects.
Coliform-Group Bacteria	A group of bacteria predominantly inhabiting the intestines of man or animal, but also occasionally found elsewhere. It includes all aerobic and facultative anaerobic, Gram-negative, non-spore-forming bacilli that ferment lactose with production of gas. Also included are all bacteria that produce a dark, purplish-green colony with metallic sheen by the membrane-filter techniques used for coliform identification. The two groups are not always identical, but they are generally of equal sanitary significance. (Ref. 26)
Colorimetry	See molecular absorption spectrophotometry.
Composite Sample	A combination of individual samples of water or wastewater taken at selected intervals, generally hourly for some specified period, to minimize the effect of the variability of the individual sample. Individual samples may have equal volume or may be proportioned to the flow at time of sampling. (Ref. 26)
Constituent	Organic or inorganic material, dissolved gas, debris or organisms present in fresh, saline or wastewater.
Contaminant	A potentially harmful pollutant or constituent.

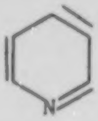
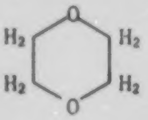
Cotton Kier Liquors	Waste liquors from cotton processing.
Detection Limit	Concentration in mg/1 that produces a reading equal to twice the standard deviation of a series of measurements near the blank level. See sensitivity.
Detritus	(1) The coarse cellular debris carried by wastewater. (2) The heavier mineral debris moved by natural watercourses, usually in bed-load form. (Ref. 26)
Dichromate Oxygen Consumed (DOC)	See COD.
Dissolved Oxygen (DO)	Oxygen present in solution in a chemically available form. In unpolluted water, oxygen is usually present in amounts of 10 μg/1 or less. Adequate dissolved oxygen is necessary for the life of fish and other aquatic organisms. About 3-5 μg/1 is the lowest limit for support of fish life over a long period of time. (Ref. 27)
Dissolved Solids (DS)	The total amount of dissolved material, organic and inorganic, contained in water or wastes. Excessive dissolved solids can make water unsuitable for industrial uses, unpalatable for drinking, and even cathartic . . . (Ref. 27) Also called Filterable Residue.
Diurnal Cycle	Daily variation in the photosynthesis-respiration pattern of aquatic flora resulting in a dissolved oxygen maximum during the day and a minimum at night -- usually just before dawn.
DPN (NAD)	Diphosphopyridine Nucleotide (nicotinamide adenine dinucleotide). A coenzyme necessary for the alcoholic fermentation of glucose.
Ecology	The science of the interrelations between living organisms and their environment.
Ecosystem	That set of ecological relationships resulting from a primary focus on an organism, group of organisms, or a portion of the earth's surface.
Effluent	(1) A liquid which flows out of a containing space. (2) Wastewater or other liquid, partially or completely treated, or in its natural state, flowing out of a reservoir, basin, treatment plant, or industrial treatment plant, or part thereof. (3) An outflowing branch of a main stream or lake. (Ref. 26)
Emergent Aquatic Plants	Plants that are rooted at the bottom but project above the water surface. Examples are cattails and bulrushes.
Endogenous	(Gr.) *endo* = within; *genesis* = growth. The growth of bacterial cultures eventually becomes *endogenous* as the result of environmental constraints imposed on the system (e.g., disappearance of nutrient substrate, enzymes, etc.).
Endogenous State	The state of continuous physiological activity in a stationary phase, which may eventually enter a declining phase.
Endpoint Filtrate COD	That point at which the filtrate COD has become constant (in the Mass Culture Aeration BOD method).
Energy Oxygen	Oxygen utilized by biota during their exponential growth phase for the synthesis of new cellular materials or biologically stable organic substances.
Environment	The sum of all external influences and conditions affecting the life and the development of an organism.

Enzyme	A class of complex proteinaceous substances produced by living cells and essential to life processes. They act similarly to catalysts in that they promote a variety of usually reversible cellular reactions (e.g., oxidation, hydrolysis) at cell temperature without themselves undergoing permanent change. Frequently the presence of activators such as metal ions or coenzymes is required for reaction to occur.
Epilimnion	That region of a body of water that extends from the surface to the thermocline and does not have a permanent temperature stratification.
Epiphyton	A non-parasitic secondary plant growth.
Estuary	Commonly an arm of the sea at the lower end of a river. Estuaries are often enclosed by land except at channel entrance points.
Eulittoral Zone	The shore zone of a body of water between the limits of water-level fluctuation.
Euphotic Zone	The lighted region that extends vertically from the water surface to the level at which photosynthesis fails to occur because of ineffective light penetration.
Eurytopic Organisms	Organisms with a wide range of tolerance to a particular environmental factor. Examples are sludgeworms and bloodworms.
Eutrophic Lake	Lake or other contained water body rich in nutrient. Characterized by a large quantity of planktonic algae, low water transparency with high dissolved oxygen in upper layer, zero dissolved oxygen in deep layers during summer months, and large organic deposits colored brown or black. Hydrogen sulfide often present in water and deposits. (Ref. 26)
Eutrophication	The normally slow aging process by which a lake evolves into marsh and ultimately becomes completely filled with detritus and disappears. In the course of this process the lake becomes overly rich in dissolved nutrients (for example, nitrogen and phosphorus), so that an excessive development of algae results. First the water becomes murky, then noxious odors and unsightly scums appear. In the lower layers dissolved oxygen levels become depressed, and bottom-dwelling fauna change from clean-water forms to pollution-tolerant forms. (Ref. 27)
Extractable Metals	The concentration of metals in an unfiltered sample following digestion with hot dilute mineral acid. (Ref. 19)
Facultative Aerobe	An organism that, although fundamentally an anaerobe, can grow in the presence of free oxygen.
Facultative Anaerobe	An organism that although fundamentally an aerobe can grow in the absence of free oxygen.
Fauna	The entire animal life of a region.
Filterable (Dissolved) Metals	Those metals which will pass through a 0.45 μm membrane filter. (Ref. 19)
Floating Aquatic Plants	Plants that wholly or in part float on the surface of the water. Examples are water lilies, water shields, and duckweeds.
Flora	The entire plant life of a region.
Formazan (Triphenyltetrazolium chloride)	A color indicator used in the quantitative estimation of oxidation-reduction equilibria involving hydrogen transfer.
F = SLR	Sludge loading ratio: Parameter used in activated sludge treatment systems to estimate imposed waste demand. It is expressed in BOD/day/lb MLVSS (Mixed liquor volatile suspended solids).

Fungi	Small non-chlorophyll-bearing plants which lack roots, stems, or leaves, which occur (among other places) in water, wastewater, or wastewater effluents and grow best in the absence of light. Their decomposition after death may cause disagreeable tastes and odors in water; in some wastewater treatment processes they are helpful and in others they are detrimental. (Ref. 26)
Fungicide	Substances or a mixture of substances intended to prevent, destroy, or mitigate any fungi. (Ref. 4)
Game Fish	Those species of fish considered to possess sporting qualities on fishing tackle. These fish may be classified as undesirable, depending on their usefulness. Examples of fresh water game fish are salmon, trout, grayling, black bass, muskellunge, walleye.
Gasometric	Pertaining to measurement of a gas parameter.
Grab Sample	A single sample of wastewater taken at neither set time nor flow. (Ref. 26)
Green Algae	Algae that have pigments similar in color to those of higher green plants. Common forms produce algal mats or floating "moss" in lakes.
Groundwater	Subsurface water occupying the saturation zone, from which wells and springs are fed. In a strict sense the term applies only to water below the water table. Also called phraetic water, plerotic water. (Ref. 26)
Hardness	A characteristic of water, imparted by salts of calcium, magnesium, and iron such as bicarbonates, carbonates, sulfates, chlorides and nitrates, that causes curdling of soap and increased consumption of soap, deposition of scale in boilers, damage in some industrial processes and sometimes objectionable taste. It may be determined by a standard laboratory procedure or computed from the amounts of calcium and magnesium as well as iron, aluminum, manganese, barium, strontium, and zinc, and is expressed as equivalent calcium carbonate. See carbonate hardness. (Ref. 26)
Herbicide	Substances or a mixture of substances intended to control or destroy any vegetation. (Ref. 4)
Herbivore	An organism that feeds on vegetation.
Heterotrophic Organisms	Organisms that are dependent on organic matter for food.
Higher Aquatic Plants	Flowering aquatic plants. (These are separately categorized as Emergent, Floating, and Submerged Aquatic Plants.)
Homeostatic Plateau	Point or place at which homeostasis occurs.
Homeostatis	(*homeo*: same; *stasis*: condition) Condition of equilibrium or stability.
Hydrology	The applied science concerned with the waters of the earth in all their states--their occurrence, distribution, and circulation through the unending hydrologic cycle of precipitation, consequent runoff, streamflow, infiltration, and storage, eventual evaporation, and reprecipitation. It is concerned with the physical, chemical, and physiological reactions of water with the rest of the earth and its relation to the life of the earth. (Ref. 26)
Hypereutrophy	Excessively enriched with nutrients. A hypereutrophic body of water may be inundated with algae, and is generally oxygen-deficient.
Hypolimnion	The region of a body of water that extends from the thermocline to the bottom of the lake and is removed from surface influence.
Immediate Dissolved Oxygen Demand (IDOD)	The OD of reduced forms of N, P, S, some metallic species and some easily oxidizable organic compounds (e.g., formaldehyde: CH_2O).
Invertebrates	Animals without backbones.

Isobestic Point	Wavelength at which the % transmission or optical density of a substance is independent of the isomeric form or oxidation state: a point of intersection for all spectral curves of the compound independent of the concentrations of its forms. For each pair of forms there will be one such isosbestic point.
Lethal Dose (LD)	A measured quantity administrated to test fish or animals. For direct feeding experiments or injections, the median toxic dosage is noted as LD_{50}, or the lethal dose for 50% of the animals. The time of observation may or may not be a criterion for single feedings or injections. (Ref. 1)
Life Cycle	The series of stages in the form and mode of life of an organism; i.e., the stages between successive recurrences of a certain primary stage such as the spore, fertilized egg, seed, or resting cell.
Limnetic Zone	The open-water region of a lake. This region supports plankton and fish as the principal plants and animals.
Limnology	The study of the physical, chemical, and biological aspects of inland waters.
Lithosphere	The outer part of the solid earth composed of rock essentially like that explored at the surface and believed to be about 50 miles in thickness.
Littoral Zone	The shoreward region of a body of water.
Macro-Organisms	Plants, animals, or fungal organisms visible to the unaided eye.
Median Lethal Dose (LD_{50})	The dose lethal to 50% of a group of test organisms for a specified period. The dose material may be ingested or injected.
Median Tolerance Limit (TL_m)	The concentration of the tested material in a suitable diluent (experimental water) at which just 50% of the test animals are able to survive for a specified period of exposure.
Membrane Filtration	A method of quantitative or qualitative analysis of bacterial or particulate matter in a water sample by filtration through a membrane capable of retaining bacteria. (Ref. 26)
Meromictic Lakes	Lakes in which dissolved substances create a gradient of density differences in depth, preventing complete mixing or circulation of the water.
Metabolizable	May be utilized by organisms in respiratory and/or growth processes.
Microorganism	Any minute organism invisible or barely visible to the unaided eye.
MLVSS	Mixed liquor volatile suspended solids.
Molecular Absorption Spectrometry (Colorimetry)	The measurement of color naturally present in samples or developed therein by the addition of reagents. (Ref. 26)
Mollusk (Mollusca)	A large animal group including those forms popularly called shellfish (but not including crustaceans). All have a soft unsegmented body protected in most instances by a calcareous shell. Examples are snails, mussels, clams, and oysters.
Moss	Any bryophytic plant characterized by small, leafy, often tufted stems bearing sex organs at the tips.
Motile	Exhibiting or capable of spontaneous movement.
Mycology	The study of fungi.
Nematoda	Unsegmented roundworms or threadworms. Some are free living in soil, fresh water, and salt water; some are found living in plant tissue; others live in animal tissue as parasites.
Nephelometer	An instrument for comparing turbidities of solutions by passing a beam of

light through a transparent tube and measuring the ratio of the intensity of the scattered light to that of the incident light. (Ref. 26)

Nitrification	Bacterial oxidation of ammonia and nitrites to nitrates.
Nutrients	Substances essential to bacterial growth and function. Chief among these are carbon, nitrogen, phosphorus, and sulfur, but a number of trace elements have been shown to be essential to growth (K, Ca, Mg, Fe, Mn, Zn, Co, Cu, and Mo). (Ref. 27)
Nonfilterable (Suspended) Metals	Those metals which are retained by a 0.45 µm membrane filter. (Ref. 19)
Oceanography	The study of the physical, chemical, geological, and biological aspects of the sea.
Oligotrophic Waters	Waters with a small supply of nutrients; thus, they support little organic production.
Organic Detritus	The particulate remains of disintegrated plants and animals. (Ref. 4)
Organic Heterocyclic Compounds	Organic ring structures containing atom(s) other than carbon (e.g., N, O, S) associated with the ring carbons. For example:  pyridine  1,4-dioxane
Osmole	The standard unit for expressing osmotic pressure. One osmole is the osmotic pressure exerted by a one-molar solution of an ideal solute.
Oxidation-Reduction Potential (ORP)	The emf developed by a platinum electrode immersed in water, referred to the Standard Hydrogen Electrode.
Oxygen Debt	A phenomenon that occurs in an organism when available oxygen is inadequate to supply the respiratory demand. During such a period the metabolic processes result in the accumulation of breakdown products that are not oxidized until sufficient oxygen becomes available.
Oxygen Tension	Partial pressure of oxygen in solution.
Partial Molal Free Energy	Free energy of a system expressed as the summation of component free energies: $$dF = \left(\frac{\partial F}{\partial T}\right) dT + \left(\frac{\partial F}{\partial p}\right) dp + \Sigma \mu_i d n_i$$
Pathogenic Bacteria	Bacteria inimical to man's welfare.
Pelagic Zone	The free-water region of a sea. (Pelagic refers to the sea, limnetic refers to bodies of fresh water.
Periphyton	The association of aquatic organisms attached or clinging to stems and leaves of rooted plants or other surfaces projecting above the bottom
Pesticide	Substances or a mixture of substances intended to prevent, destroy or repel plant or animal pests. (Ref. 26)
Photometer	An instrument that measures the intensity of light or the degree of light absorption. (Ref. 26)
Photosynthesis	The process by which simple sugars and starches are produced from carbon

	dioxide and water by living plant cells, with the aid of chlorophyll and in the presence of light.
Phototrophism	Movement in response to a light gradient; for example, a movement towards light is *positive* phototrophism.
Phytoplankton	Plant plankton that live unattached in water.
Piscicide	Substances or a mixture of substances intended to destroy or control fish populations
Plankton (Plankter)	Aquatic organisms of relatively small size mostly microscopic, that have either relatively small powers of locomotion or that drift in the water with waves, currents, and other water motion.
Poising Index	The increment of oxidizing agent (in equivalents/ℓ) divided by the incremental change in Eh. A measure of the electrical stability of a system subjected to ORP measurement.
Polarography	Automatic electroanalysis of a solution, usually by means of the dropping mercury electrode, by measuring current flow with voltage changes. (Ref. 26)
Pollutant	The term "pollutant" refers to any matter discharged into a body of water, or entering it from the air or soil, which is not normally a component of that particular ecosystem. The pollutant in question may, or may not, result in immediately obvious deleterious changes in the aquasystem.
Pollution	". . . the accidental or intentional discharge, directly or indirectly, of any liquid, gaseous, thermal and/or solid substance into water. These added pollutants may constitute a nuisance or be actually injurious to the health and well-being of man, animals, birds, and aquatic life forms such as fish and plants." (Ref. 72a, BOD)
Pollution (of Water)	Contamination or other alteration of the physical, chemical, or biological properties of water, including changes in temperature, taste, color, or odor of the water, or the discharge into the water of any liquid, gaseous radioactive, solid, or other substance that may create a nuisance or render such water detrimental or injurious to public health, safety, or welfare. Broadly, pollution means any change in water quality that impairs it for the subsequent user. (Ref. 27)
Pool Zone	The deep-water area of a stream, where the velocity of current is reduced. The reduced velocity provides a favorable habitat for plankton. Silt and other loose materials that settle to the bottom of this zone are favorable for burrowing forms of benthos.
Porifera	See Sponges.
Potable Water	Water that does not contain objectional pollution, contamination, minerals, or infective agents and is considered satisfactory for domestic consumption. (Ref. 26)
Potassium Dichromate ($K_2Cr_2O_7$)	Oxidizing agent commonly used in the determination of *Chemical Oxygen Demand (COD)*. In acid solution this salt is reduced from Cr^{+6} to the Cr^{+3} valence state in the presence of organic and/or inorganic reducing agents. The color change from yellow (Cr^{+6}) to green (Cr^{+3}) forms the basis of a spectrophotometric analytical method of COD determination.
Potassium Permanganate ($KMnO_4$)	Oxidizing agent formerly employed in COD analyses. In this country it has been largely superseded by the (silver catalyzed) dichromate procedure.

Precision	(1) Relative or apparent nearness to the truth. In physical measurements, it should not be confused with accuracy, which denotes absolute nearness to the truth. (2) In analytical chemistry, a measure of the reproducibility of a method when repeated on a homogeneous sample, regardless of whether the observed values are widely displaced from the true value as a result of systematic or constant errors present throughout the measurements. It may be expressed in terms of the standard deviation. (Ref. 2 and 26)
Producers	Organisms, for example, plants, that synthesize their own organic substances from inorganic substances.
Production (Productivity)	A time-rate unit of the total amount of organism grown.
Profundal Zone	The deep and bottom-water area beyond the depth of effective light penetration. All of the lake floor beneath the hypolimnion.
Protozoa	Organism consisting either of a single cell or of aggregates of cells, each of which performs all the essential functions in life. They are mostly microscopic in size and largely aquatic
Rapids Zone	The shallow-water area of a stream, where velocity of current is great enough to keep the bottom clear of silt and other loose materials, thus providing a firm bottom. This zone is occupied largely by specialized benthic or periphytic organisms that are firmly attached to or cling to a firm substrate.
Receiving Waters	The bodies of water that receive effluent wastewater from treatment plants.
Red Tide	A visible red-to-orange coloration of an area of the sea caused by the presence of a bloom of certain "armored" flagellates.
Redd	A type of fish-spawning area associated with running water and clean gravel. Fish moving upstream sequentially dig a pocket, deposit and fertilize eggs and then cover the spawn with gravel from the next upstream pocket. Fishes that utilize this type of spawning area include some trouts, salmons, and minnows.
Reducers	Organisms that digest food outside the cell wall by means of enzymes secreted for this purpose. Soluble food is then absorbed into the cell and reduced to a mineral condition. Examples are fungi, bacteria, protozoa, and nonpigmented algae.
Rheotropism	Movement in response to the stimulus of a current gradient in water.
Riffle	A section of a stream in which the water is usually shallower and the current of greater velocity than in the connecting pools; a riffle is smaller than a rapid and shallower than a chute.
Rotifers (Rotatoria)	Microscopic aquatic animals, primarily free-living, fresh water forms that occur in a variety of habitats. Approximately 75% of the known species occur in the littoral zone of lakes and ponds. The more dense populations are associated with the presence of submerged aquatic vegetation. Most forms ingest fine organic detritus for food, whereas others are predaceous.
Saline Water	Water containing dissolved salts -- usually from 10,000 to 33,000 mg/l. (Ref. 26)
Salinity	The weight in vacuo of solids which can be obtained when all organic matter has been oxidized, all bromides and iodides have been replaced by chlorides, all carbonates converted to oxides and the residue has been dried to constant weight at 480°C with appropriate correction for loss of volatile halide during drying.
Scavenger	An organism that feeds upon decomposing organic matter.

Scuds (Amphipods)	Macroscopic aquatic crustaceans that are laterally compressed. Most are marine and estuarine. Dense populations are associated with aquatic vegetation. Great numbers are consumed by fish.
Secchi Disc	A device used to measure visibility depths in water. The upper surface of a circular metal plate, 20 centimeters in diameter, is divided into four quadrants and so painted that two quadrants directly opposite each other are black and the intervening ones white. When suspended to various depths of water by means of a graduated line, its point of disappearance indicates the limit of visibility.
Sediment	(1) Solid material settled from suspension in a liquid. (2) Mineral or organic solid material that is being transported or has been moved from its site of origin by air, water, or ice and has come to rest on the earth's surface either above or below sea level. (3) Inorganic or organic particles originating from weathering, chemical precipitation, or biological activity. (Ref. 26)
Seed	Viable organisms, usually obtained from settled sewage, and known to be effective in promoting oxidation of organics. Seeding is generally carried out prior to the BOD measurement of effluents containing bio-inhibitors.
Self Purification	(a) The partial or complete restoration by natural processes, of a stream's pristine condition following the introduction of foreign matter sufficient in quality and quantity to cause a measurable change in physical, chemical and/or biological characteristics. Lee defined self-purification in terms of reactions producing "transformations that result in the production of a chemical compound that has a less deleterious effect on water quality than the parent compound." He divided reactions into 8 types: acid-base, precipitation, gas transfer, complex formation, oxidation-reduction, photochemical reactions, sorption, and biochemical reactions. (Ref. 39, vol. 1, chapter 4, BOD) (b) Process whereby a stream rids itself of impurities, generally forfeiting DO.
Sensitivity	Concentration in mg/l that produces a reading of 1%. The term is used often in metals analysis. See detection limit. (Ref. 19)
Sessile Organisms	Organisms that sit directly on a base without support, attached or merely resting unattached on a substrate.
Shellfish Poison (Mussel Poison)	A poison present in shellfish that have fed upon certain small marine phytoplankters in which the toxic principles exist. The shellfish concentrates the poison without harmful effects to itself, but man is poisoned through consumption of the toxic flesh.
Sludge	(1) The accumulated solids separated from liquids, such as water or wastewater, during processing, or deposits on bottoms of streams or other bodies of water. (2) The precipitate resulting from chemical treatment, coagulation, or sedimentation of water or wastewater. (Ref. 26)
Sludge Bulking	Flocculation: problem which arises in the Activated Sludge (AS) treatment of wastes.
Sludge Loading Ratio (SLR)	Parameter used in AS treatment systems. It is expressed in lbs BOD/day/1b MLVSS.
Specific Conductance (of Water)	Measure of a water's capacity to convey an electric current. This property is related to the total concentration of the ionized substances in the water and the temperature of the water. Most inorganic acids, which dissociate readily in aqueous solution, will conduct an electric current well, while organic compounds (such as sucrose and benzene), which do not dissociate in aqueous solution, will conduct a current poorly if at all. (Ref. 27)

Spectrophotometry	Quantitative measurement with a photometer of the quantity of light of any specific wavelength absorbed by a colored solution or emitted by a sample excited by a flame, arc, or spark. (Ref. 26)
Sphaerotilus	(a) A genus of bacteria having filaments that exhibit false branching, and reproducing by both conidia and swarmers. (b) A slime-producing, nonmotile, sheathed, filamentous, attached bacterium. Great masses are often broken from their "holdfasts" by currents and are carried floating downstream in gelatinous flocks.
Sponges(Porifera)	One of the sessile animals that fasten to piers, pilings, shells, rocks, etc. Most live in the sea.
Spore	The reproductive cell of a protozoan, fungus, alga, or bryophyte. In bacteria, spores are specialized resting cells.
Spring Overturn	A physical phenomenon that may take place in a body of water during the early spring. The sequence of events leading to spring overturn include: (1) melting of ice cover, (2) warming of surface waters, (3) density change in surface waters producing convection currents from top to bottom, (4) circulation of the total water volume by wind action, and (5) vertical temperature equality. The overturn results in a uniformity of the physical and chemical properties of the water.
SS	Suspended solids.
Stabilization Oxygen Demand	Oxygen consumed in energy reactions through the point where death of microorganisms is essentially complete and only relatively stable organic end products remain
Standing Crop	The biota present in an environment on a selected date.
Stenotopic Organisms	Organisms with a narrow range of tolerance for a particular environmental factor. Examples are trout, stonefly nymphs, etc.
STOD	Short Term Oxygen Demand.
STP	Standard temperature & pressure (0°C, 760 mm).
Sublittoral Zone	The part of the shore from the lowest water level to the lower boundary of plant growth.
Submerged Aquatic Plant	A plant that is continuously submerged beneath the surface of the water. Examples are the pondweed and coontail.
Surface Water	(1) All water on the surface, as distinguished from ground water. (2) Water appearing on the surface in a diffused state, with no permanent source of supply or regular course for any considerable time, as distinguished from water appearing in watercourses, lakes, or ponds. (Ref. 26)
Suspended Solids	Solids suspended in waste water. The amount of suspended solids is a measure of the strength of sewage. (Ref. 27)
Swimbladder	An internal, membranous, gas-filled organ of many fishes. It may function as a hydrostatic or sense organ, or as part of the respiratory system.
Swimmers' Itch	A rash produced on bathers by a parasitic flatworm in the cercarial stage of its life cycle. The organism is killed by the human body as soon as it penetrates the skin; however, the rash may persist for a period of about 2 weeks.
Symbiosis	Two organisms of different species living together, one or both of which may benefit and neither is harmed.

Systematics	The science of organism classification.
TBOD	Total Biological Oxygen Demand
Thermocline	That layer in a body of water where the temperature difference is greatest per unit depth. It is the layer in which the drop in temperature equals or exceeds 1°C (1.8°F) per meter (39.37 inches).
TL_m	See Median Tolerance Limit.
TOD	Total Oxygen Demand.
Tolerance Limit (TL)	Term used in designating a level of any measurable lethal agent, including physical parameters such as high and low temperatures, pH, and the like. As an example, a bioassay 96-hour TL_{50} of a toxic substance is that concentration in which 50% of the fish survive for 96 hours. TL_{50} is equivalent to the median tolerance limit (TL_m). (Ref. 2)
Tolerant Association	An association of organisms capable of withstanding adverse conditions within the habitat. It is usually characterized by a reduction in species (from a clean water association) and an increase in individuals representing a particular species.
Total Metals	The concentration of metals determined on an unfiltered sample following vigorous digestion or the sum of the concentrations of metals in both the filterable and nonfilterable fractions. (Ref. 19)
Toxic	Poisonous; deleterious to the survival of living organisms (see median tolerance limit).
Toxic Substance	A substance that either directly poisons living things or alters their environment so that they die. Examples are cyanides found in plating and steel mill wastes, phenols from coke and chemical operations, pesticides and herbicides, and some heavy metal salts. Another broad group includes oxygen-consuming substances that upset the balance of nature, such as organic matter from food plants, pulp and paper mills, chemical plants, and textile plants. Still another group are sulfides, produced by oil refineries, smelters, and chemical plants. (Ref. 27)
TPTZ	Triphenyltetrazolium chloride -- see Formazan.
Trickling Filter	Rock or gravel bed used in the treatment of sewage.
Trophogenic Region	The superficial layer of a lake in which organic synthesis from mineral substances occurs in the presence of light energy.
Tropholytic Region	The deep layer of a lake, where organic dissimilation predominates because of light deficiency.
Turbidimeter	An instrument for measurement of turbidity, in which a standard suspension usually is used for reference. (Ref. 26)
Turbidity	An empirical measure of the optical property of the particles of mud, clay, silt, finely divided organic matter, or microscopic organisms suspended in water that interfere with light transmission, causing the light to be scattered and absorbed rather than transmitted through the water in straight lines. (Ref. 27)
Ultimate Biochemical Oxygen Demand	The relatively stable end products from stabilization oxygen demand slowly continue to be degraded. The ultimate achievement of essentially complete oxidation to CO_2, water, and inorganic end products is termed the ultimate biochemical oxygen demand.
Ultimate Carbonaceous BOD	The maximum value attainable by complete oxidation of all organic constituents in the solution.
Vertebrate	Animals with backbones.

Virus	The smallest (10-300 mμ in diameter) form capable of producing infection and diseases in man or other large species. Occurring in a variety of shapes, viruses consist of a nucleic acid core surrounded by an outer shell (capsid) which consists of numerous protein subunits (capsomeres). Some of the larger viruses contain additional chemical substances. The true viruses are insensitive to antibiotics. They multiply only in living cells where they are assembled as complex macromolecules utilizing the cells' biochemical systems. They do not multiply by division as do intracellular bacteria. (Ref. 26)
Virtually Absent	The subject constituent is present in very low concentrations, and is not objectionable in these barely detectable concentrations. (Ref. 4)
VSS	Volatile suspended solids.
Warm and Cold-Water Fish	Warm-water fish include black bass, sunfish. catfish, gar and others; whereas cold-water fish include salmon and trout, whitefish, miller's thumb, and blackfish. The temperature factor determining distribution is set by adaptation of the eggs to warm or cold water.
Wastewater	The spent water of a community. From the standpoint of source, it may be a combination of the liquid and water-carried wastes from residences, commercial buildings, industrial plants, and institutions, together with any groundwater, surface water, and storm water that may be present. In recent years, the word wastewater has taken precedence over the word sewage. (Ref. 26)
Water	(1) A transparent, odorless, tasteless liquid, a compound of hydrogen and oxygen, H_2O, freezing at 32° F or 0° C and boiling at 212° F or 100° C, which in more or less impure state, constitutes rain, oceans, lakes, rivers, and other such bodies; it contains 11.188 percent hydrogen and 88.812 percent oxygen, by weight. It may exist as a solid, liquid, or gas and, as normally found in the lithosphere, hydrosphere, and atmosphere, may have other solid, gaseous, or liquid materials in solution or suspension. (2) To wet, supply, or irrigate with water. (Ref. 26)
Waterfleas (Daphnia)	Mostly microscopic swimming crustaceans, often forming a major portion of the zooplankton population. The second antennae are very large and are used for swimming.
Water Quality	The chemical, physical, and biological characteristics of water with respect to its suitability for a particular purpose. The same water may be of good quality for one purpose or use, and bad for another, depending on its characteristics and the requirements for the particular use.
Zooglea	Bacteria embedded in a jellylike matrix formed as the result of metabolic activities.
Zooplankton	Protozoa and other animal microorganisms living unattached in water. These include small crustacea, such as daphnia and cyclops.

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J. APPENDIX A

Narrative Notes for Table 2

(Reproduced from Water Quality Criteria, Report of the National Technical Advisory Committee to the Secretary of the Interior, Federal Water Pollution Control Administration (1968) available from U.S. Government Printing Office, Washington, DC 20402.

Paragraph 1: Color

A limit of 75 color units (platinum-cobalt standard) has been recommended to permit the defined plant to produce water meeting Drinking Water Standards (*10*) with moderate dosages of coagulant chemicals. At optimum pH the dosage usually required is linearly related to the color of the raw water, and higher color of the type commonly associated with swamp drainage and similar nonindustrial sources can be removed by increasing the coagulant dose. These criteria do not apply to colors resulting from dyes and some other industrial and processing sources which cannot be measured by the platinum-cobalt* standard. Such colors should not be present in concentrations which cannot be removed by the defined method of treatment.

Paragraph 2: Odor

The effectiveness of the defined method of treatment in removing odorous materials from water is highly variable depending on the nature of the material causing the odor. For this reason, it has not been feasible to specify any permissible criterion in terms of threshold odor number. The raw water should not have objectionable odor. Any odors present should be removable by the defined treatment. It is desirable that odor be virtually absent.

Paragraph 3: Temperature

Surface water temperatures vary with geographical location and climatic conditions. Consequently no fixed criteria are feasible. However, any of the following conditions are considered to detract (sometimes seriously) from raw water quality for public water supply use:

(1) Water temperature higher than 85 F;
(2) More than 5 F water temperature increase in excess of that caused by ambient conditions;
(3) More than 1 F hourly temperature variation over that caused by ambient conditions;
(4) Any water temperature change which adversely affects the biota, taste, and odor, or the chemistry of the water;
(5) Any water temperature variation or change which adversely affects water treatment plant operation (for example, speed of chemical reactions, sedimentation basin hydraulics, filter wash water requirements, etc.);
(6) Any water temperature change that decreases the acceptance of the water for cooling and drinking purposes.

Paragraph 4: Turbidity

Turbidity in water must be readily removable by coagulation, sedimentation, and filtration; must not be present in quantities (either by weight or volume) that will overload the water treatment plant facilities; and must not cause unreasonable treatment costs. In addition, turbidity in water must not be frequently changing and varying in characteristics or in quantity to the extent that such changes cause upset in water treatment plant processing.

Customary methods for measuring and reporting turbidity do not adequately measure those characteristics harmful to public water supply and water treatment processing. A water with 30 Jackson turbidity units may coagulate more rapidly than one with 5 or 10 units. Similarly water with 30 Jackson turbidity units sometimes may be more difficult to coagulate than water with 100 units. Sometimes clay added to very low turbidity water will improve coagulation. Therefore, it has not been possible to establish a turbidity criterion in terms of Jackson turbidity units. Neither can a turbidity criterion be expressed in terms of mg/l "undissolved solids" or "nonfilterable solids." The type of plankton, clay, or earth particles, their size and electrical charges, are far more determining factors than the Jackson turbidity units. Nevertheless, it must be clearly recognized that too much turbidity or frequently changing turbidity is damaging to public water supply.

The criterion for too much turbidity in water must relate to the capacity of the water treatment plant to remove turbidity adequately and continuously at reasonable cost. Water treatment plants are designed to remove the kind and quantity of turbidity to be expected in each water supply source. Therefore, any increase in turbidity and any fluctuating turbidity load over that normal to a water must be considered in excess of that permissible.

Paragraph 5: Coliform and Fecal Coliform Organisms

Bacteria have been used as indicators of sanitary quality of water since 1880 when *B. coli* and similar organisms were shown to be normal inhabitants of fecal discharges. The coliform group as presently recognized by Drinking Water Standards (*10*) is defined in Standard Methods for the Examination of Water and Wastewater (*9*). This group includes organisms that vary in biochemical and serologic characteristics and in their natural sources and habitats; i.e., feces, soil, water, vegetation, etc.

Because the sanitary significance of the various members of the coliform group derives from their natural sources, differentiation of fecal from non-fecal organisms is important to evaluate raw water quality (*5*). Fecal coliforms are characteristically inhabitants of warmblooded animal intestines. Members of other coliform subgroups may be found in soil, on plants and insects, in old sewage, and in waters polluted some time in the past.

The objective of using the coliform group as an indicator of the sanitary quality of water is to evaluate the disease-producing potential of the water. To estimate the probability of pathogens being contributed from feces, the coliform and fecal coliform content must be quantified.

In relation to raw water sources, the following suggestions are offered to help resolve some of the difficulties of data interpretation.

Fecal coliform organisms may be considered indicators of recent fecal pollution. It is necessary to consider all fecal coliform organisms as indicative of dangerous contamination. Moreover, no satisfactory method is currently available for differentiating between fecal organisms of human and animal origin.

In the absence of fecal coliform organisms, the presence of other coliform group organisms may be the result of less recent fecal pollution, soil runoff water, or, infrequently, fecal pollution containing only those organisms.

In general, the presence of fecal coliform organisms indicates recent and possibly dangerous pollution. The presence of other coliform organisms suggests less recent pollution or contributions from other sources of non-fecal origin.

In the past the coliform test has been the principal criterion of suitability of raw water sources for public water supply. The increase in chlorination of sewage treatment plant effluents distorts this criterion by reducing coliform concentrations without removing many other substances which the defined water treatment plant is not well equipped to remove. It is essential that raw water sources be judged as to suitability by other measures and criteria than coliform organism concentrations.

The defined water treatment plant is considered capable of producing water meeting Drinking Water Standards (*10*) bacteriological criteria from these limits. The difference between the suggested concentration of 10,000 coliforms per 100 ml and the erstwhile figure of 5,000 per 100 ml is justified by the difference between the Phelps Index and the MPN. The Subcommittee suggests these numbers and the additional consideration of fecal coliforms in order to provide more realistic parameters in full recognition of modern knowledge and not as a means of sanctioning increased bacterial pollution of waters destined for public water supply use.

Paragraph 6: Alkalinity

Alkalinity in water should be sufficient to enable floc formation during coagulation, must not be high enough to cause physiological distress in humans, and must be proper for a chemically balanced water (neither corrosive nor incrusting). A criterion for minimum and maximum alkalinity in public water supply is related to the relative amounts of bicarbonates, carbonates, and hydroxide ions causing the alkalinity; and also to the pH, filterable (dissolved) solids, and calcium content. Because the permissible criterion for filterable solids is 500 mg/l and the pH range is 6.0 to 8.5, alkalinity should not be less than about 30 mg/l.

The criterion for maximum alkalinity cannot be expressed in calcium carbonate equivalents as determined from 0.02N H_2SO_4 titration because of the interrelationships stated above. However, alkalinity values higher than about 400 mg/l to 500 mg/l would be too high for public water supply use. Within the range of 30 mg/l to 500 mg/l, the alkalinity criterion should be that value which is normal to the natural water and which from experience is satisfactory for public water supply use. Frequent variations from normal values are detrimental to public water supply processing control.

Paragraph 7: Ammonia

Ammonia is a significant pollutant in raw water for public water supplies because its reactions with chlorine result in compounds with markedly less disinfecting efficiency than free chlorine. In addition, it is frequently an indicator of recent sewage pollution.

In the early days of waste treatment, the oxidation of ammonia to nitrates was one of the major objectives of waste treatment, but with the development of the BOD test, this objective became neglected. Greater attention to the design and operation of waste treatment plants for the oxidation of ammonia and organic nitrogen is needed to minimize the concentration of pollution forms in these receiving waters.

Paragraph 8: Arsenic, Barium, Cadmium, Chromium (Hexavalent), Copper, Chloride, Cyanide, Iron, Lead, Manganese, Phenols, Selenium, Silver, Sulfate, Zinc, and Radioactive Substances

The significance of these substances as contaminants of drinking water is discussed in Drinking Water Standards (*10*). The permissible criteria in this report are those included in Drinking Water Standards. With the possible exception of iron and in some instances copper and zinc, the defined treatment plant does little or nothing to

Paragraph 9: Boron

Boron is found in the natural ground and surface waters in some areas of the United States, notably in the Western States where as much as 5 to 15 mg/l are encountered. However, extensive data on boron in both well and surface waters in North America show that the amount of boron normally encountered is less than 1 mg/l. The ingestion of large amounts of boron can affect the central nervous system and protracted ingestion may result in a clinical syndrome known as borism.

Boron is an essential element to plant growth but is toxic to many plants at levels as low as 1 mg/l. The Public Health Service has established a limit of 1 mg/l which provides a good factor of safety physiologically and also considers the domestic use of water for home gardening.

Paragraph 10: Dissolved Oxygen

Criteria for dissolved oxygen are included, not because the substance is of appreciable significance in water treatment or in finished water, but because of its use as an indicator of pollution by organic wastes. It is intended for application to freeflowing streams and not to lakes or reservoirs in which supplies may be taken from below the thermocline.

Paragraph 11: Fluoride

The Subcommittee recognizes the potential beneficial effects of fluoride ion in domestic water supplies but recommends no "desirable" concentration since any value less than that recommended for the permissible limit would be acceptable from the point of view of a water pollution control program. Rapid fluctuations in raw-water fluoride ion levels would create objectionable operating problems for communities supplementing raw-water fluoride concentrations. The permissible criterion is the upper limit of the recommended range in Drinking Water Standards (*10*).

Annual average of Maximum daily air temperatures[1] F:	Recommended Limit mg/l
50.0 to 53.7	1.7
53.8 to 58.3	1.5
58.4 to 63.8	1.3
63.9 to 70.6	1.2
70.7 to 79.2	1.0
79.3 to 90.5	0.8

[1] Based on temperature data obtained for a minimum of 5 years.

Paragraph 12: Hardness

A singular criterion for the maximum hardness in public water supply is not possible. Hardness in water is largely the result of geological formations with which the water comes in contact. Public acceptance of hardness varies from community to community. Consumer sensitivity to objectionable hardness is related to the hardness with which he has become accustomed. Consumer acceptance of hardness may also be tempered by economic necessity.

Hardness should not be present in concentrations that will cause excessive soap consumption, or which will cause objectionable scale in heating vessels and pipes. In addition, varying water hardness is objectionable to both domestic and industrial water consumers. With varying hardness, the soap required for laundry, the effect on manufactured products, and the damage to process equipment (such as boilers and cooling coils) cannot be anticipated and compensated without facilities which are not available to most water users. A water hardness criterion must relate to the hardness which is normal to the supply and exclude hardness additions which will cause variations.

A criterion for objectionable hardness must be tailored to fit the requirements of each community. Hardness more than 300–500 mg/l as $CaCO_3$ is excessive for public water supply. Many consumers will object to water harder than 150 mg/l. In other communities, the criterion for maximum water hardness is considerably less than 150 mg/l. A moderately hard water is sometimes defined as having hardness between 60 to 120 mg/l.

Paragraph 13: Nitrate plus Nitrite

A limit of 10 mg/l(N) of nitrate ion plus nitrite ion will be recommended by Drinking Water Standards (*10*). Because the nitrite ion is the substance actually responsible for causing methemoglobinemia, a combined limit on the two ions is more significant than a limit on nitrates only.

Paragraph 14: pH

Most unpolluted waters have pH values within the range recommended as a permissible criterion. Any pH value within this range is acceptable for public water supply. The further selection of a specific pH value within this range as a desirable criterion cannot be made.

Paragraph 15: Phosphorus

The Subcommittee has considered establishing criteria on phosphorus concentrations but has not been able to establish any generally acceptable limit because of the complexity of the problem. The purpose of such a limit would be twofold:

(a) To avoid problems associated with algae and other aquatic plants, and
(b) To avoid coagulation problems due particularly to complex phosphates.

Phosphorus is an essential element for aquatic life as well as for all forms of life and has been considered the most readily controllable nutrient in efforts to limit the development of objectionable plant growths. Evidence indicates that high phosphorus concentrations are associated with the eutrophication of waters that is manifest in unpleasant algal or other aquatic plant growths when other growth-promoting factors are favorable; that aquatic plant problems develop in reservoirs or other standing waters at phosphorus values lower than those critical in flowing streams; that reservoirs and other standing waters will collect phosphates from influent streams and store a portion of these within the consolidated sediments; that phosphorus concentrations critical to noxious plant growths will vary with other water quality characteristics, producing such growths in one geographical area but not in another.

Because the ratio of total phosphorus to that form of phosphorus readily available for plant growth is constantly changing and will range from two to 17 times or greater, it is desirable to establish limits on the total phosphorus rather than the portion that may be available for immediate plant use. Most relatively uncontaminated lake districts are known to have surface waters that contain 10 to 30 μg/l total phosphorus as P; in some waters that are not obviously polluted, higher values may occur (*4*). Data collected by the Federal Water Pollution Control Administration, Division of Pollution Surveillance, indicate that total phosphorus concentrations exceeded 50 μg/l (P) at 48 percent of the stations sampled across the Nation (*6*). Some potable surface water supplies now exceed 200 μg/l (P) without experiencing notable problems due to aquatic growths. Fifty micrograms per liter of total phosphorus (as P) would probably restrict noxious aquatic plant growths in flowing waters and in some standing waters. Some lakes, however, would experience algal nuisances at and below this level.

Critical phosphorus concentrations will vary with other water quality characteristics. Turbidity and other factors in many of the Nation's waters negates the algal-producing effects of high phosphorus concentrations. When waters are detained in a lake or reservoir, the resultant phosphorus concentration is reduced to some extent over that in influent streams by precipitation or uptake by organisms and subsequent deposition in fecal pellets or dead organism bodies. See the report of the Subcommittee for Fish, Other Aquatic Life, and Wildlife, and the section on Plant Nutrients and Nuisance Organisms for a more complete discussion of phosphorus associations with the enrichment problem.

At concentrations of complex phosphates of the order of 100 μg/l, difficulties with coagulation are experienced.

Paragraph 16: Total Dissolved Solids (Filterable Residue)

Drinking Water Standards (*10*) recommend that total dissolved solids not exceed 500 mg/l where other more suitable supplies are available. It is noted, however, that some streams contain total dissolved solids in excess of 500 mg/l. For example, the Colorado River at the point of withdrawal by the Metropolitan Water District of Southern California has a total dissolved solids concentration up to 700 mg/l.

High total dissolved solids are objectionable because of physiological effects, mineral taste, or economic effect. High concentrations of mineral salts, particularly sulfates and chlorides, are associated with corrosion damage in water systems. Regarding taste, on the basis of limited research work underway in California, limits somewhat higher than 500 mg/l are probably acceptable to consumers of domestic water supplies. It is likely that levels set with relation to economic effects are controlling for this parameter.

Increases in total dissolved solids from those normal to the natural stream are undesirable and may be detrimental.

It is recommended that the permissible value for total dissolved solids be set at 500 mg/l in view of the above evaluation. Further, it is recommended that research work be sponsored to obtain more information on total dissolved solids in water relating to physiological effects, consumer attitudes toward taste, and economic considerations.

Paragraph 17: Uranyl Ion

The standard for uranyl ion ($UO_2^{=}$) is established on the basis of its chemical properties rather than on the basis of its being a radioactive material. It is being added to Drinking Water Standards (*10*). Uranyl ion is of concern in drinking water because of possible damage to the kidneys. The threshold level of taste and the appearance of color due to uranyl ion occur at about 10 mg/l which is much less than the safe limit of ingestion of this ion insofar as adverse physiological effects are concerned.

The Public Health Service adopted the figure of 5 mg/l which is one-half the limit based on taste and color and, therefore, there is a considerable factor of safety in the adoption of 5 mg/l.

Paragraph 18: Carbon Chloroform Extract (CCE)

A limit of 0.2 mg/l carbon chloroform extract in drinking water is recommended in the Drinking Water Standards "as a safeguard against the intrusion of excessive amounts of potentially toxic material into water" (*10, 3*). Although the analytical procedure then in use leaves much to be desired from the standpoint of simplicity, reproducibility, and interpretation, it was the best available at that time. The analytical procedure has been improved since then and the newer technique (*1, 2*) gives substantially higher results than the one originally used. The defined method of treatment generally removes very little of the CCE present in the raw water. In many instances there is an increase during treatment. Whether this is real or apparent is not known.

The permissible criterion of 0.15 mg/l recommended is based on use of the procedure cited in Drinking Water Standards (*10*). We do not as yet have sufficient information on which to base a recommended limit using the lower flow rates and sample volumes of the newer procedure. When this information is available, a change in the criterion is advisable. This limit is generally attainable where vigorous efforts at pollution control are carried out.

Paragraph 19: Methylene Blue Active Substances

This is an operationally more precise name for substances discussed in Drinking Water Standards (*10*) as alkyl benzene sulfonate. The permissible criterion is the same as the limit recommended in those standards. Those standards have been revised to reflect this change in nomenclature.

Paragraph 20: Oil and Grease

It is very important that water for public water supply be free of oil and grease. The difficulty of obtaining representative samples of these materials from water makes it virtually impossible to express criteria in numerical units. Since even very small quantities of oil and grease may cause troublesome taste and odor problems, the Subcommittee desires that none of this material be present in public water supplies. An additional problem attributable to these agents is the unsightly scumlines on water treatment basin walls, swimming pools, and other containers.

Paragraph 21: Pesticides and Herbicides

Consideration was given by the Subcommittee to three groups of pesticides: the more common chlorinated hydrocarbons, herbicides, and the cholinesterase-inhibiting group which include the organic phosphorus types and the carbamates. The permissible levels are based upon recommendations of the Public Health Service Advisory Committee on Use of the PHS Drinking Water Standards. These values were derived for that Committee by an expert group of toxicologists as those levels which, if ingested over extensive periods, could not cause harmful or adverse physiological changes in man. In the case of aldrin, heptachlor, chlordane, and parathion, the Committee adopted even lower than physiologically safe levels; namely, amounts which, if present, can be detected by their taste and odor. It should be noted that this National Technical Advisory Subcommittee on Public Water Supplies is not a group of toxicological experts. Hence, the promulgation of additional criteria by the Public Health Service would also be accommodated by this Subcommittee, tempered—as was done above—by its experience and judgment in the area of water treatment, as, for example, in public acceptance of organoleptic properties.

The limit for the cholinergic pesticides is established relative to parathion and is expressed as 0.1 mg/l parathion equivalent. This equivalence is the ratio that a given pesticide of this group has to parathion as unity in its cholinesterase inhibiting properties. This makes it incumbent upon an administrator of this limit to determine the pesticide involved and to obtain expert toxicological opinion on its parathion equivalence. Nearly all the organophosphorus compounds and the cholinergic carbamates have high acute toxicity to mammals and some have even higher toxicity to fish. Ingestion of small quantities of these compounds over long time periods causes damage to mammalian central nervous systems. Many organophosphorus pesticides hydrolyze rapidly in the environment to harmless or less harmful products. The hazards from the chlorinated hydrocarbon pesticides in water results from both direct effects, because they tend to persist in their original form over long periods, and indirect effects because they may be concentrated biologically in man's food chain. The values which were selected by the Public Health Service as limits for this group of pesticides are, however, set with substantial safety factors insofar as they adversely affect the human body. Generally, fish are more sensitive to this group of pesticides and, therefore, may serve as a rough method for determining when the chlorinated hydrocarbon pesticides content of water is approaching a danger level. See the report of the Fish, Other Aquatic Life, and Wildlife Subcommittee for pesticide limits relative to maintaining healthy and productive aquatic life.

It should be noted that limits for pesticides and herbicides have been set with relation only to human intake directly from a related domestic water supply. The consequence of higher and possibly objectionable concentrations in fish available to be eaten by man due to biological concentration is considered not within the scope of the charge to this Subcommittee.

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8

APPENDIX B

Toxic Pollutant Effluent Standards

(Reproduced from Federal Register, Vol. 38, No. 173--Friday, September 7, 1973).

SUBCHAPTER D—WATER PROGRAMS

PART 129—TOXIC POLLUTANT EFFLUENT STANDARDS

List of Toxic Pollutants

On July 6, 1973, notice was published in the FEDERAL REGISTER (38 FR 18044) that the Environmental Protection Agency was proposing a list of toxic pollutants pursuant to section 307(a)(1) of the Federal Water Pollution Control Act, as amended (33 U.S.C.A. section 1317(a) Supp 1973), (the Act) which provides in part:

> The Administrator shall, within ninety days after the date of enactment of this title, publish (and from time to time thereafter revise) a list which includes any toxic pollutant or combination of such pollutants for which an effluent standard (which may include a prohibtion of the discharge of such pollutants or combination of such pollutants) will be established under this section.

That proposed list included aldrin-dieldrin, benzidine, cadmium, cyanide, DDT (DDE, DDD), endrin, mercury, polychlorinated biphenyls, and toxaphene.

Written comments on the proposed rulemaking were invited and received from interested parties and are on file with the Agency. All comments have been considered by the Environmental Protection Agency and certain ones have been adopted. These and other principal changes are discussed below.

Several comments dealt with the manner in which the inorganic components of the list were specified and argued that certain insoluble or innocuous forms of these substances should not be included in broad categories such as "all cadmium compounds." Effluent standards which must be developed for the listed pollutants will include analytical and sampling procedures which will distinguish between the toxic and innocuous forms of the designated pollutants.

A number of commenters expressed the opinion that the proposed selection criteria were vague and inadequate. It was obvious from the comments received that a great deal of confusion existed as to what materials could potentially be selected as toxic pollutants.

Accordingly, EPA has refined these criteria to make them more specific. These criteria entail two major advantages. First, they will provide for more informed public participation, by identifying the kinds of pollutants which the Agency proposes to examine and the types of data which are sought for each pollutant. Second, dischargers will be placed on notice concerning the class of pollutants which may become subject to standards under Section 307(a).

It is our intent that the process of selecting pollutants for the list of toxic pollutants will be a continuing one; as additional evidence is developed, additional pollutants will be added to the list.

Pollutants were chosen for inclusion on the initial list in light of the following criteria:

1. Data from laboratory or field studies indicate that the pollutant could, if discharged into water, constitute a serious environmental threat. The types of data examined in making this judgment are set forth in Part I below.
2. The pollutant is discharged, or has the potential to be discharged, from point sources and constitutes a very serious environmental threat.
3. Data are available to establish effluent standards meeting the requirements of the Act.
4. Standard setting under Section 307 (a) is appropriate, and is necessary because the prospective timing and effectiveness of abatement actions under other provisions of the Act are not commensurate with the nature and seriousness of the problems identified by the above criteria.

I. EXPLANATION OF CRITERIA

The first criterion concerns the actual or potential damage that a water discharge of these materials may create by virtue of certain toxicological properties.

Detailed toxicological data are examined to determine whether one or more of these types of effects are known: bioaccumulation, carcinogenic, mutagenic and teratogenic effects, and high acute toxicity. Specifically, the following types of data are reviewed:

1. Available data concerning whether a substance or its chemical or biological transformation product is bioaccumulated through an aquatic mechanism to the extent that they result in:

(a) Reproductive impairment in any important species, or

(b) Concentrations in food sources in excess of applicable Federally established tolerance levels.

2. Data concerning carcinogenic, mutagenic, and teratogenic effects. Materials likely to be carcinogenic, mutagenic, or teratogenic to man are further evaluated as to their chemical, biological, and physical stability in water.

3. Data concerning high order of

toxicity as measured by short-term lethality tests. In this connection a classification of a substance as "highly toxic" to man according to classifications established by the Department of Transportation and the Environmental Protection Agency (36 FR 2934, February 12, 1971, 40 CFR 162.8) and the Environmental Protection Agency and the Food and Drug Administration testing procedures (40 CFR 162.8 and 21 CFR 191.10) is particularly relevant. According to the references cited above, substances which have an oral LD50 of 50 mg/kg of body weight or less or have a dermal LD50 of 200 mg/kg of body weight of less are defined as highly toxic to mammals and are examined further. The term "oral LD50" means that single oral dose which is lethal to one-half of the test population within 14 days. The term "dermal LD50" means that dose dermally absorbed in 24 hours which is lethal to one-half of the test population within 14 days.

For the protection of aquatic life, substances proposed to be classified as "highly toxic" according to the National Academy of Sciences water pollution ranking system may be considered for inclusion in the list. Such substances are those which are toxic to aquatic life as measured by a 96 hour LC50 of 10 mg/l or less. The term "LC50" means that concentration of a substance in water which is lethal to one-half of the test population in the specified time periods. Testing methods such as those found in "Standard Methods for the Examination of Water and Wastewater," 13th Edition, part 231, 1971, or their equivalent will be considered adequate.

The second criterion concerns the seriousness of discharges or potential discharges of the pollutant from point sources. Relevant here are such factors as the nature and extent of toxic effects associated with the pollutant, the extent to which discharges of the pollutant have been identified, and the production, distribution, and use pattern of the pollutant. Data must be available from well documented field studies showing damage to important organisms from discharges of the compound into waters, or technically sufficient to show the material has the potential to be environmentally harmful after being discharged from point sources to the water.

The third criterion concerns setting effluent standards for pollutants on the list. The following are representative of the categories of data useful in standard setting for each material.

1. Toxicity to man and other organisms;
2. Carcinogenicity, mutagenicity, and teratogenicity data;
3. Transport paths of the material in the environment;
4. Bioaccumulation and bioconcentration;
5. Chemical, physical, and biological transformations in the environment;
6. Reliability and accuracy of analytical procedures;
7. Chemical characteristics;
8. Production and industrial or commercial utilization;
9. Sources of the pollutant to water;
10. Environmental incidents attributable to the material (fish kills, etc.);
11. Presence of the material in the environment, residue levels in various organisms, ambient concentrations in rivers, lakes, etc.;
12. State and Federal regulatory requirements concerning the material;
13. Classes and characteristics of waters into which the material is discharged.

The fourth criterion concerns the overall environmental effect of the control measures available, including the use of substitute products, and possible effects upon ground water or other environmental media.

II. THE POLLUTANTS SELECTED

The emergency standards promulgated by the Department of Labor for occupational carcinogens (38 FR 10929, May 3, 1973), have forced a shift in the manufacture of benzidine from the previous producers to the end users. The resulting potential for increased water pollution by this known carcinogen and the adverse effects on the environment which may result, require the listing of benzidine. Public comments have indicated that the material should be included, and that discharges should be severely controlled. Other public comments indicated that the material does not meet the selection criteria as proposed July 6, 1973. Benzidine does meet the criteria set forth herein. It was also asserted that the DOL standards would protect both the work place and the environment. However, those standards are designed to prevent occupational exposure, not to control discharges into water.

Mercury is on the list because its organic form is known to bioaccumulate to the extent that it poses a threat to the health of man through concentration in food sources, so as to exceed applicable tolerance levels. Control of point source discharges is urgently needed, and available data are sufficient for standard setting. Public comments noted that the discharge of this material should be severely restricted. Some comments were received recommending deletion of the material from the list because of questions of solubility and demethylation of mercury and its compounds. It should be noted, however, that all forms of mercury in the aquatic environment can be methylated to methylmercury, the most hazardous form.

Aldrin-dieldrin are on the list because of their high order of toxicity to aquatic organisms and their bioaccumulative properties. Control is necessary now and there are adequate data to support effluent standards. Some comments indicated that aldrin-dieldrin should be deleted because of possible conflict with on-going cancellation proceedings under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). The Administrator has an obligation to control toxic pollutants under FWPCA which is independent of his authority under FIFRA. These responsibilities cannot be abdicated. Moreover, it is too early to ascertain the precise determinations which will be required under the FWPCA, and the impact on the FIFRA proceedings. Accordingly, deletion of aldrin-dieldrin is not considered to be warranted at this time.

Cadmium is included on the list because of toxicity to aquatic organisms. From our studies, it was determined that there are several hundred dischargers of cadmium, and controls are urgently needed. Public comment supported the inclusion of this material because of its high order of toxicity to aquatic organisms, potential concentrations in the food web, and its widespread discharge. Some commenters objected to the inclusion of "Cadmium and all cadmium compounds" on the list because some relatively innocuous forms of the element would be included. The final effluent standards will distinguish among the various forms in which the element may occur.

DDT, DDD, and DDE are on the list because of their acute toxicity to aquatic organisms, and their bioaccumulative properties, which are known to cause harmful effects in higher life forms, such as birds. The data are sufficient for the establishment of effluent standards. Public response in favor of inclusion of DDT, DDD, and DDE noted the existence of much data on the harmful effects of these materials. One commenter stated that DDD degrades rapidly, and does not have many of the effects associated with DDT. It was determined, however, that DDD should also be included because of its toxicity and bioaccumulative properties.

Endrin is highly toxic to aquatic life at low concentrations. Considerable data are available on endrin, and control of point sources is necessary at present. Those public comments that supported its inclusion cited considerable data, and urged stringent control. One commenter alleged that the sole manufacturing facility is under control, and that further restriction is unnecessary and redundant. However, available technical and scientific data support inclusion. Moreover, the manufacturer of the material is not the only point source, since formulators also contribute endrin contaminated wastes to the environment.

Polychlorinated biphenyls are on the list because of their high order of toxicity to man and aquatic organisms, and because of their bioaccumulative potential. The data are adequate, and the point source discharges require prompt control. Public comments indicated that the materials should be included because of their widespread use, and their demonstrated harm to aquatic life. These commenters urged that discharges be as low as possible. No comments were received recommending deletion of polychlorinated biphenyls.

Toxaphene is on the list because of its high order of toxicity to aquatic life. Considerable data are available concerning this compound, and prompt control of known point sources is required. Public comments in support of the material being included cited much of the available toxicity data. Some commenters argued that this material did not meet the selection criteria published in connection with the proposed list of July 6, 1973. Toxaphene does meet the criteria set forth in this notice.

Since toxaphene has infrequently been reported to be present in the environment, some commenters urged its deletion. However, controls are necessary because the material continues to be manufactured, formulated, and distributed in large quantities. Thus, the potential for harmful discharges is considerable.

Cyanide is on the list because of its high order of toxicity to aquatic life. There are many different types of point source discharges and a variety of receiving bodies of water which must be protected from the discharge of this material. The data are adequate to support effluent standards. The public commenters in favor of inclusion cited data on toxicity to aquatic life in very low concentrations. Those commenters who recommended deletion for the most part objected to inclusion of "all cyanide compounds." It was argued that only compounds which dissociate in water to form toxic concentrations of cyanide ion or hydrogen cyanide should be included. The proposed effluent standards will take these comments into account, and may specify special sampling, analysis, and reporting requirements.

III. THE LENGTH OF THE LIST

Several commenters recommended that the final list include a larger number of pollutants than were included on the proposed list. In addition, a number of commenters requested shortening the list. Most of the latter recommended removal of specific pollutants; these recommendations have been discussed in the preceding section.

As required by section 515 of the Act,

EPA notified the Effluent Standards and Water Quality Information Advisory Committee on June 6, 1973, of our intention to propose effluent standards for toxic pollutants under section 307(a). The Committee held hearings on the proposed list in Washington, D.C. (July 16), Chicago, Ill. (July 30), New York, N.Y. (August 1), and San Francisco, Calif. (August 3). The Committee has agreed to provide scientific and technical information concerning the listed pollutants, but has made no recommendations to date concerning the length of the list.

Pursuant to the consent decree entered into by EPA in the case of *NRDC v. Fri*, Civ. Action No. 849-73 (D.D.C.), EPA must publish proposed standards for all pollutants included on this initial list no later than December 3, 1973.

Additional toxic pollutants lists may be published in the future under section 307(a). The Agency will examine a wide range of pollutants in constituting such lists. Among those which will be examined are the following pollutants which were identified in public comments on the initial list:

arsenic
selenium
chromium
lead
asbestos
sevin
zinc
chlordane
lindane
acridine
hydroquinone
ortho-chlorophenol
beta-naphthol
alpha-naphthol
beryllium
nickel
antimony
heptachlor
camphor
methyl parathion
parathion
di-n-butyl phthalate

The Agency will examine other pollutants in addition, including chlorinated hydrocarbons, organophosphates, heavy metals, and materials listed as occupational carcinogens by the Department of Labor (38 FR 10929, May 3, 1973).

Persons interested in assisting the Environmental Protection Agency in setting standards for the pollutants listed in Section IV are invited to submit scientific and technical data, and other information concerning the listed pollutants, to Dr. C. Hugh Thompson, Chairman, Hazardous and Toxic Substance Regulation Task Force, Office of Water Program Operations, Environmental Protection Agency, Washington, D.C. 20460. In particular, the thirteen categories of standard-setting data set forth in Section I above are sought for all pollutants listed in Section IV. The Agency is also interested in obtaining data on technology for waste control treatment and disposal of the pollutants listed in Section IV.

In addition, the Agency will review any data submitted on pollutants proposed to be placed on future lists. The pollutants listed above are merely representative of pollutants identified in public comment which may be candidates for selection. Data on those pollutants, and on other pollutants which may be candidates for selection, should be submitted to the Chairman, Hazardous and Toxic Substance Regulation Task Force, at the address set forth in the preceding paragraph.

Dated August 31, 1973.

JOHN QUARLES,
Acting Administrator.

IV. THE LIST OF TOXIC POLLUTANTS

Pursuant to section 307(a) of the Federal Water Pollution Control Act, as amended, effluent standards will be established for the pollutants listed below:

1. Aldrin (1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4,5,8 endo-exodimethanonaphthalene).
   Dieldrin (1,2,3,4,10,10-hexachloro 6,7-epoxy - 1,4,4a,5,6,7,8,8a - octahydro - 1,4 - endo,exo-5,8-dimethanonaphthalene).
2. Benzidine and its salts (para-para'-diaminobiphenyl).
3. Cadmium and all cadmium compounds.
4. Cyanide and all cyanide compounds.
5. DDD (TDE) 1,1 - dichloro - 2,2 - bis(para-chlorophenyl)-ethane.
   DDE(dichlorodiphenyldichloroethylene) 1,1 - dichloro-2,2 - bis(para-chlorophenyl) ethylene.
   DDT(dichlorodiphenyltrichloroethane) 1,1,1 - trichloro-2,2-bis(para-chlorophenyl) ethane.
6. Endrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a - octahydro - 1,4 - endo - endo-5,8-dimethanonaphthalene).
7. Mecury and all mercury compounds.
8. Polychlorinated biphenyls (PCB's).
9. Toxaphene (chlorinated camphene).

[FR Doc.73-19018 Filed 9-6-73;8:45 am]

APPENDIX C

(Reproduced from Federal Register, Vol. 40, No. 51, March 14, 1975, Page 11990).

ENVIRONMENTAL PROTECTION AGENCY

[40 CFR Part 141]

[FRL 343-8]

PRIMARY DRINKING WATER

Proposed Interim Standards

Notice is hereby given that pursuant to sections 1412, 1414, 1415 and 1450 of the Safe Drinking Water Act ("the Act," Pub. L. 93–523) the Administrator of the Environmental Protection Agency (EPA) proposes to issue a new 40 CFR Part 141 setting forth interim primary drinking water standards (Subpart A) and regulations governing the granting of variances and exemptions from those standards (Subpart B). The proposed regulations set forth below cover only the interim primary standards. Proposed regulations dealing with the granting of variances and exemptions will be published shortly.

The Act was signed by the President on December 16, 1974. It is the first Federal Act dealing in depth with providing safe drinking water for public use. The standards proposed today are the first regulations to be published as part of EPA's implementation of this new major environmental legislation. Under section 1412(a)(1) of the Act, EPA is obligated to publish proposed standards within 90 days after enactment, and promulgation of final standards is required 180 days after enactment. Those standards become effective 18 months after the date of their promulgation.

The Act clearly contemplates that the States, rather than the Federal government, will have primary responsibilities for carrying out the purposes of the legislation. Thus, when a State demonstrates that it has the authority and capability to carry on a program consistent with the Act, the Federal government will recognize the State's primary enforcement responsibilities and will thereafter play largely a passive role in assuring safe drinking water in that State. Under section 1413(a)(1) of the Act a State has primary enforcement responsibility if the Administrator has determined that such State—

(1) Has adopted drinking water regulations which

(A) In the case of the period beginning on the date the National Interim Primary Drinking Water Regulations are promulgated under section 1412 and ending on the date such regulations take effect are no less stringent than such regulations, and

(B) In the case of the period after such effective date are no less stringent than the interim and revised national primary drinking water regulations in effect under such section;

(2) Has adopted and is implementing adequate procedures for the enforcement of such State regulations, including conducting such monitoring and making such inspections as the Administrator may require by regulation;

(3) Will keep such records and make such reports with respect to its activities under paragraphs (1) and (2) as the Administrator may require by regulation;

(4) If it permits variances or exemptions, or both, from the requirements of its drinking water regulations which meet the requirements of paragraph (1), permits such variances and exemptions under conditions and in a manner which is not less stringent than the conditions under, and the manner in, which variances and exemptions may be granted under sections 1415 and 1416; and

(5) Has adopted and can implement an adequate plan for the provision of safe drinking water under emergency circumstances.

The Administrator shall, by regulation (proposed within 180 days of the date of the enactment of the Act, prescribe the manner in which a State may apply to the Administrator for a determination that the requirements of paragraphs (1), (2), (3), and (4) of subsection (a) of section 1413 of the Act are satisfied with respect to the State, the manner in which the determination is made, the period for which the determination will be effective, and the manner in which the Administrator may determine that such requirements are no longer met. Such regulations shall require that before a determination of the Administrator that such requirements are met or are no longer met with respect to a State may become effective, the Administrator shall notify such State of the determination and the reasons therefor and shall provide an opportunity for public hearing on the determination. Such regulations shall be promulgated (with such modifications as the Administrator deems appropriate) within 90 days of the publication of the proposed regulations in the FEDERAL REGISTER. The Administrator shall promptly notify in writing the chief executive officer of each State of the promulgation of regulations under this paragraph. Such notice shall contain a copy of the regulations and shall specify a State's authority under this title when it is determined to have primary enforcement responsibility for public water systems.

(2) When an application is submitted in accordance with the Administrator's regulations, the Administrator shall within 90 days of the date on which such application is submitted

(A) Make the determination applied for, or

(B) Deny the application and notify the applicant in writing of the reasons for his denial.

Within 180 days after enactment EPA is required to propose regulations which prescribe the manner in which a State may apply to the Administrator for a determination that it has met the criteria for operation of a safe drinking water program.

A principal concern of EPA in determining the scope, stringency, and timing of the proposed interim drinking water regulations is the burden they will impose and its implications for the workability of the regulations. The Act assigns a predominant role to the States. EPA recognizes that decisions to implement these regulations on the part of most States must be a reasonable probability. The willing cooperation of subordinate levels of government, public utilities and others is also necessary. In this regard, commenters are urged to keep in mind the levels of dollar resources and other assistance that can be expected from EPA to support States, local government and other participants in carrying out the Act. EPA's budget request for grants to States for public water system supervision programs in FY 1976 is $7,500,000. EPA personnel resources and other financial resources will be made available, particularly to assist the States in setting up and operating programs, to the extent possible, but this support will necessarily be limited and the States and utilities will need to allocate funds to implement the program.

EPA has provided for phasing in the testing requirements in the presently proposed regulations. In its regulations governing the requirements for State programs to qualify for primary enforcement responsibility EPA will allow considerable leeway in the time-phasing of programs, and will permit considerable variation and flexibility in State approaches to enforcement. Even so, many impacts and duties will fall upon the States as soon as these regulations are effective eighteen months after promulgation. Enforcement requests and citizens suits must be anticipated to commence then. Calls for State assistance to localities and utilities, including extensive laboratory services and approval of laboratories, assistance in upgrading performance and other services, will escalate. Violations of the regulations by suppliers of water will become immediately apparent with the operation of section 1414(c) of the Act and § 141.32 of the regulations as to public notification. A flow of applications for variances and exemptions will begin.

With these considerations in mind, yet recognizing the overriding consideration of improving protection of public health through assuring compliance with the standards set forth in these regulations, EPA must fix the maximum contaminant levels and other requirements called for in the interim regulations. On the many aspects of this most important issue involving the appropriate balance of health protection and realistic implementation of the program, EPA requests public analysis and comment.

The Interim Primary Drinking Water Standards proposed today protect health to the extent feasible, taking costs into consideration, using technology, treatment techniques and other means generally available. The Act in section 1401 requires that for each primary drinking water contaminant the Administrator specify either a maximum contaminant level if it is feasible to ascertain that level in water, or, a treatment technique which leads to a sufficient reduction in the level of such contaminant if it is not feasible to ascertain that level. Based on past monitoring experience for these levels, the Administrator has determined that it is economically and technologically feasible to monitor drinking water for contaminants at the maximum contaminant levels. Therefore, required treatment techniques will not be a part of these interim primary standards. However, EPA welcomes comment on this issue and if public comment justifies it, EPA will consider issuing treatment techniques in lieu of maximum contaminant levels for one or more of the contaminants covered in the regulations.

The interim primary standards proposed today are based largely on the 1962 Public Health Service Drinking Water Standards and the review of those standards accomplished by the EPA Advisory Committee Report on the Revision and Application of the Drinking Water Standards, as recommended to the Administrator, on September 20, 1973.

The Act in section 1412(b) provides that revised primary drinking water standards are to be proposed (and promulgated within 180 days thereafter) 100 days following the date of the report on the study to be conducted by the National Academy of Sciences on recommended health-based maximum contaminant levels. This report is due no later than December 16, 1976. In turn, the revised primary regulations will be effective 18 months following the date of their promulgation. While it is anticipated that changes will be made in some of the maximum contaminant levels of the interim primary standards, that there will be contaminants added to the list of regulated substances, and that broad groupings of contaminants (such as organics) will be further defined, the revised standards will not automatically supersede the interim standards. Only if the revised regulations expressly revoke the interim standards will the latter no longer be effective. In determining whether the revised regulations will supersede, the Administrator will consider the length of time they have been in effect, and the compatibility of the compliance strategies and techniques for meeting interim and revised regulations. If all or part of the interim regulations remain in effect, the water supplier will be required to meet both sets of standards sequentially.

Definitions and coverage. To determine whether these standards apply to a particular system, reference must be made to both §§ 141.2 and 141.3 of the regulations. The term "public water system" is defined in § 141.2(e) to mean a system which serves at least fifteen service connections or at least twenty-five individuals on a regular basis. Public water systems which otherwise would be covered by the Act are not required to meet these standards if they serve 25 or more people but only for less than three months out of the year. The intent is to cover campgrounds and resort facilities which may serve for at least three months a substantial population. Although a supplier of drinking water must comply with all requirements of the Act when he is providing water, he need not monitor, make reports, etc., while the system is not operating or when it is regularly providing water to fewer than twenty-five individuals.

For a public water system to be excluded from coverage by these regulations it must meet all four criteria set out by § 141.3.

The broad definition of "State" in § 141.2(f) is intended to make clear that the State government is the primary enforcement authority if the State has assumed this authority under section 1413 of the Act; if not, the Regional Administrator of EPA is the primary enforcement authority. The only exception is found in § 141.31 (Reporting Requirements), where the Federal Agencies are required to report results of analyses to the Regional Administrator even when the State has assumed primary enforcement responsibility.

Maximum contaminant levels. The maximum contaminant levels for Arsenic, Barium, Cadmium, Chromium, Cyanide, Fluoride, Lead, Selenium and Silver are identical to the 1962 Drinking Water Standards (section 5.22). With the exception of nitrates, all of the maximum contaminant levels for inorganic chemicals are based upon data addressed to possible health effects that may occur after a lifetime of exposure, and the standards have been reviewed in light of substantial information generated since the publication of the 1962 Standards. More complete summaries of the bases for these standards are contained in the Statement of Basis and Purpose.

Special attention is invited to the cadmium standard. Recent evidence has established that cigarette smoking may contribute as much or more cadmium to the body burden as does the ingestion of cadmium with food. The standard for cadmium proposed today does not take into account the additive effect of cadmium ingestion from smoking. EPA invites comments as to the question whether the cadmium standard should be directed specifically toward protection of smokers as well as non-smokers.

Only a small fraction of the mercury in drinking water is in the alkyl form, which is considered more toxic than other forms of mercury. Alkyl mercury has only been detected in water in the nanogram per liter range. However, the proposed standard for mercury is derived on the assumption that all mercury in water is methyl mercury. Public comment is solicited as to whether or not this procedure is reasonable. Possible alternatives include:

a. Setting the standard on the assumption that all the mercury in the water is methyl mercury, but requiring that the total mercury concentration be below the specified level,

b. Leaving the standard at the present level to protect against the toxic effects of methyl mercury, but specify that the standard applies only to that form, or

c. Establishing two standards—one for organic and one for inorganic mercury.

The maximum contaminant level for organic chemicals (§ 141.12) is determined by the Carbon Chloroform Extract (CCE) procedure employing the low flow Carbon Adsorption Method (CAM-low flow) sampler. The present interim primary standard (0.7mg/1–CAM-low flow) is substantively equivalent to the 1962 Standard (0.2 mg/1–CAM-high flow). The low flow CAM sampler provides longer contact time between the water sample and the activated carbon and therefore, has 3½ times greater extraction efficiency.

EPA is conducting several monitoring surveys (including the National Reconnaissance Survey of drinking water supplies mandated by the Act) to determine the extent of the incidence of organic chemicals in drinking water and associated toxicity of those substances. Revised standards will reflect the results of those studies.

The pesticide contaminants listed in the proposed regulations issued today were not contained in the 1962 Standards. The maximum contaminant levels for these substances have been derived from the recent data on effects of acute and chronic exposure to both organochlorine and chlorophenoxy pesticides.

The list of pesticide contaminants does not include Aldrin/Dieldrin and DDT because the Agency is presently conducting an intensive nationwide survey to determine the extent of the contamination of the drinking water by these persistent pesticides. This program is to be completed within the next few months, and subsequently the Agency will propose interim primary drinking water standards for Aldrin/Dieldrin and DDT. Almost all uses of DDT were cancelled under the Federal Insecticide, Fungicide and Rodenticide Act, 7 U.S.C. 136 et seq., on March 18, 1971, and the Agency has suspended the major uses of Aldrin/Dieldrin (October 1, 1974, 39 FR 37272). (This suspension is presently on appeal to the United Statese Court of Appeals for the District of Columbia Circuit, Nos. 74–1924, 74–2113, and 74–2114). A factor in both actions was evidence that those pesticides are potential carcinogens. The interim primary drinking water standards for these chemicals will take this evidence of carcinogenicity into account.

The Administrator has also issued a notice of intent to cancel many of the major uses of heptachlor and chlordane, which are included in these standards. Heptachlor epoxide, though not a product directly applied as a pesticide, results from the use of heptachlor or chlordane. Preparations are underway for presentation at an adjudicatory hearing the evidence relating to the carcinogenic risks associated with the use of heptachlor and chlordane. It is anticipated that the maximum contaminant levels for heptachlor, chlordane, and heptachlor epoxide—which are based on chronic human toxicity other than carcinogenicity—will be reviewed within the next several months and may be revised to reflect the cancer risk which may be inherent in their presence in drinking water.

In planning new or expanded water supply systems in the next few months, owners should be aware that the National Academy of Sciences, and National Academy of Engineering in "Water Quality Criteria," 1972, have recommended that the following concentrations not be exceeded in sources of water to be used for drinking water:

Aldrin	0.001 mg/l
DDT	0.05 mg/l
Dieldrin	0.001 mg/l

It is unlikely that EPA will issue interim primary drinking water standards which permit concentrations in finished water in excess of these values.

Organophosphate insecticides have been considered for inclusion in these standards. However, there are not sufficient data related to their occurrence in drinking water or raw water sources to warrant setting standards at this time. Although these substances are widely used in agriculture, they are not usually intentionally added to watercourses; the possible pathways to water supplies are indirect, such as through percolation, runoff from treated lands, and accidental spills. Many organophosphate insecticides are almost completely degraded within days in water partially explaining the fact that the intact organophosphates are seldom detected in water.

It must be emphasized, however, that most organophosphate insecticides are Class I poisons. Therefore, authorities should be cautioned that accidental spills or misuse of these substances might demand immediate attention similar to that required with any type of acute acting contaminant that enters our nation's water. The use of section 1431 of the Act, or State law modeled upon it, may also be appropriate in such situations. A guidance manual entitled "Policies and Procedures for Review and Evaluation of Toxicity in Drinking Water of Chemicals other than Coagulant Aids" is available for use in these situations from the Water Supply Research Laboratory, National Environmental Research Center, U.S. Environmental Protection Agency, 4676 Columbia Parkway, Cincinnati, Ohio 45268.

The interim primary drinking water standards proposed today have a limit for turbidity (§ 141.14) because turbidity in water interferes with disinfection efficiency and because high turbidity often signals the presence of other health hazards. The growth of microorganisms in a distribution system is often stimulated if excessive particulate or organic matter is present. The supplier is allowed to have no greater than five turbidity units in the water (rather than one) when he can show that an effective disinfectant agent is present in the system in sufficient concentrations to protect the water users.

The standards for microbiological contaminants are contained in § 141.15. The maximum levels are in terms of the surrogate coliform bacteria, although the purpose of the standard is to protect against disease-causing bacteria, viruses, protozoa, worms and fungi. The analytical procedures for direct detection of these microorganisms are not well enough developed nor practicable for widespread application at this time. Total coliform counts have been used for nearly 100 years as indicators because the organisms are present in large quantity in the intestinal tracts of humans and other warm blooded animals, thus the number remaining in a water supply provides a good correlation with sanitary significance.

To ease the economic burden on the smaller systems, these standards provide in § 141.16 that chlorine residual concentrations may be measured and substituted for a portion of the bacteriological samples. This alternative is based on the assumption that chlorine in proper concentrations will destroy those organisms which are indirectly being measured by the coliform test. Small systems (serving 4900 or fewer people) may make a total substitution, but it should be noted that several chlorine samples are required for each substituted microbiological sample, and a higher chlorine residual must be maintained in the system.

Interim Primary Drinking Water Standards for radiological substances are not included in the regulations proposed today. The Agency intends to publish proposed radiological maximum contaminant levels and analytical and sampling requirements in the near future.

Almost all of the maximum contaminant levels are based on an assumed consumption of two liters of water per day. The question arises, however, as to whether or not it is reasonable to derive the drinking water standards on the basis of the average amount of water consumed by any large segment of the population (in the case of these standards, young adult American males) since a large portion of the members of that class consume more.

EPA solicits information as to whether or not the present approach is reasonable, and whether there is any available information regarding the distribution of water consumption levels by significant segments of the American public.

Sampling and analytical requirements. Sections 141.21–141.24 set out the sampling and analytical requirements to be followed in determining whether there is compliance with the maximum contaminant levels. Section 141.21 establishes the monitoring frequency for the microbiological contaminants. When there is an apparent violation noted, the supplier is directed to accelerate the sampling from the same monitoring point until the results indicate that the maximum contaminant level is no longer exceeded. The requirement to step up the monitoring is not in lieu of the reporting and notification responsibilities which arise when there is a violation. Also, the "check samples" required by § 141.21(c)(1)–(c)(3) are not to be included in the calculations of the total samples taken each month for the purposes of determining compliance with § 141.21(b).

A violation of § 141.16 is deemed to occur when a second properly conducted test, which must be run within one hour of the first test, shows that the chlorine concentration is below the specified level. The required sample for coliform analysis must be taken at the point where the violation in the chlorine residual was detected.

The sampling frequency for turbidity determination (§ 141.22) differs for supplies drawing water from underground sources and for surface water supplies. It is presumed that the likelihood of high turbidity in water from underground sources is relatively small.

Section 141.23 sets forth the requirements for inorganic chemical sampling and analyses. Within one year from the effective date of this subpart the supplier must make one analysis for inorganic chemicals; subsequent analyses must be performed yearly if the system does not primarily serve transients. Less frequent analyses are required for suppliers drawing water from underground sources. If this level of an inorganic chemical is greater than 75 percent of the maximum contaminant level, the supplier is directed to re-analyze monthly.

The sampling frequencies for the inorganic chemicals, organic chemicals and pesticides allows considerable time within which the supplier may take the first sample, due to the limited number of laboratories capable of making the often difficult analyses. Public water suppliers are encouraged to begin monitoring for these substances even before the effective date of this subpart. Any analyses made in accordance with the analytical procedures set forth in this subpart but before the effective date can be considered when determining compliance with §§ 141.23 and 141.24.

To assure confidence in analytical results, which in many cases the public water suppliers will contract for, a section has been added to provide for laboratory certification (§ 141.27).

Reporting requirements. A key provision of these proposed standards is the reporting requirement (§ 141.31). Within 40 days following an analysis required by subpart A, the results must be reported to either the State or the Regional Administrator, depending on who has primary enforcement responsibility.

Federal Agencies will at all times report to the Regional Administrator, although they must follow State agency substantive standards if the State agency has assumed primary enforcement responsibility.

If a standard is based upon averaging of samples, the report must be filed within 40 days of the first sample used in the averaging. If there is a violation, whether based on averaging or a single analysis with one check analysis, the report must be received within 36 hours of the finding of violation. The reports of violations of the standards include reports of instances where the monitoring requirements have not been followed.

One of the basic assumptions embodied in the Safe Drinking Water Act is that if the public is aware that the drinking water being provided is below Federal Standards, they will request the local officials to remedy the situation. Thus § 141.32 of these Standards is intended to carry out the statutory directive that the public served by the public water system be adequately informed of the quality of the water they are receiving. The supplier must give notice of failure to meet the requirements of § 141.32 by publication in a newspaper or newspapers, by promptly giving a copy of the notice to the TV and radio stations serving the area, and by inclusion of the notice in the water bills. Failure to follow the required monitoring requirements is deemed a violation equal to failure to meet a maximum contaminant level.

Public water suppliers are allowed as part of the notice to the public to give fair explanation of the public health significance of any violation, or of any variance or exemption, which the supplier must report as required by subsection (b) of § 141.31.

The Agency anticipates that additions may be made to the public notification provision to differentiate between the type of notice required in the case of emergencies and that provided for in § 141.31.

Siting requirements. The siting requirements of § 141.41 are designed to assure that, to the extent practicable, the location of the intake and other elements of new or expanded water supply systems will be such that the public water systems will be able to provide a continuous supply of healthful drinking water. To the extent practicable, facilities should be located in areas not subject to floods, earthquakes, fires, or other disasters. Section 141.41 is not intended to give EPA veto authority over new public water systems, although State agencies may have this power. In all cases there must be notification of the State or Regional Administrator that construction of a new or expanded system is contemplated.

Economic, energy, and chemical considerations. Economic, energy, and chemical factors have been considered in the development of the Proposed Interim National Primary Drinking Water Standards. In establishing the phased monitoring schedule, the maximum contaminant levels themselves, and the notification requirements, every effort has been made to identify costs and to keep them within the bounds contemplated by Congress.

The estimates contained herein are based on data currently available and should be considered preliminary. The data include the 1969 Community Water Supply Study published by the U.S. Public Health Service in July 1970. In addition, EPA has also conducted several pilot studies of water supplies of several Federal agencies, i.e., U.S. Forest Service, Corps of Engineers, Bureau of Reclamation, National Park Service, and Interstate Highways to evaluate the status and condition of supplies serving the travelling public. Until EPA's inventory of community water supplies is completed and adequate data are obtained on the capability of each system, the full impact of these proposed interim regulations will not be known. EPA is undertaking a more comprehensive analysis of the overall impact of the proposed standards and does expect to have more definitive estimates to present when it promulgates the interim standards. EPA expects and invites comments on the economic impact of these regulations in order that the final regulations presented are both reasonable and practical.

The preliminary cost estimates do not appear excessive or inflationary. The estimated replacement value of the 40,000 community (resident) water systems is $125 billion; annual monitoring costs for the community water systems would be less than 0 [illegible] percent of this value and capital costs to bring the systems up to compliance levels would be about 1 percent of this value.

Estimated costs are based on the needs of 40,000 systems serving resident populations and 200,000 supplies serving nonresident populations. These costs, however, relate only to the construction and operation of facilities to enable water supply systems to meet the health related constituent limits that are established in these Interim Primary Regulations. This excludes any costs to provide for growth of population served and to provide for the removal of taste and/or odor problems or any other aesthetic desires. The monitoring costs for all community supplies are estimated to be $20 million the first year and to increase to $30 million after 5 years. Costs during intervening and subsequent years will vary slightly due to phasing and annual frequency of monitoring requirements. Capital costs for upgrading these systems are estimated to be about $1,400 million, which will result in an annual cost of $365 million.

For the supplies serving non-resident populations, monitoring costs will vary from $45 million the first year to $60 million the fifth year. The capital cost for upgrading these systems will be approximately $6 million. It should be noted that the other (non-resident) capital costs relate only to those pertaining to meeting only the proposed bacteriological limits. Most of the chemical limits in the proposed regulations were set with a view to chronic effects resulting from lifetime exposures. Since these systems serve a transient population, the need to attain the proposed chemical limits may be questionable. The economic consequences could impose severe hardship on these small systems and the granting of variances and exemptions by the States may be justified. No effort was made to calculate the annual cost related to these systems, since operating and maintenance costs are not known at this time.

The implementation costs are summerized in the following table:

[Dollars in millions]

Annual monitoring	Community (resident)	Other (Non-residential)	Total
Costs:			
1st year	$20	$45	$65
5th year	30	60	90
Upgrading costs:			
Capital costs	1,400	6	
Annual costs	[1] 365		

[1] Includes operation and maintenance.

Health costs have not been included in these estimates, although improved water quality will undoubtedly have a beneficial effect on health costs. Studies are underway to determine these costs, and they will be integrated as soon as possible.

It should be noted that the total annual monitoring costs do give credit to the bacteriological monitoring that is being performed today. For example, 700 of the estimated 40,000 community water systems are currently subject to Federal purview, under the interstate quarantine regulations of the Public Health Service Act. These systems, which include many of the major cities in the country, serve a resident population of 85 million, or more than half of the population served by community systems. For these systems bacteriological monitoring is now adequate and in fact some chemical monitoring is also being performed.

A potential major cost-reducing factor not included in these figures is expanded control by EPA over effluents of the listed contaminants. EPA is currently examining the implications of controlling pollutants at the source of discharge into the water. In effect, by controlling the pollutants at their source, EPA will be reducing the direct economic burden on the public sector.

The energy requirements to operate the added facilities and to produce the chemicals for clarification (alum, lime, etc.) constituent removal (sulfuric acid, activated carbon, etc.) and disinfection are estimated at 21 billion BTU's annually or .025 percent of the current estimate for the 1975 national energy consumption of 80 quadrillion BTU's.

The chemical requirements related to the additional treatment required by the proposed standards are summarized below:

Chemical requirements

Chemical	Pounds (10)	Percent of annual production
Filter grade alum	370	16 (1973)
Activated carbon	7	4 (1972)
Lime	421	1 (1972)
Chlorine gas	167	0.8 (1973)
Sulphuric acid	473	0.8 (1973)
Sodium hydroxide	77	0.4 (1973)

Alum and activated carbon will apparently require significant portions of current total production. These chemicals are used in large part for water treatment and the raw materials are abundant. Therefore it is not believed that significant problems will be involved in increasing their production in the long term.

Impact on State Programs. With particular regard to the potential impact of the proposed regulations on State programs, EPA is anxious to have comprehensive comments and data on costs and administrative burden generally, as well as on feasibility of State program implementation in light of dates scheduled for the effectiveness of the regulations. Specifically, EPA requests data to show the costs to the States that will follow from the testing requirements imposed by these regulations on public water systems, from the requirement that public water systems report test results to the States, and from the requirement that tests must be conducted by laboratories approved by the States. EPA will consider such cost information as is supplied prior to promulgating final Interim Primary Drinking Water Standards as well as considering such data and information in the development of proposed State Program regulations, section 1421, which is scheduled for issuance in mid June 1975.

Comments and public hearings. EPA presented draft Interim Primary Drinking Water Standards to the National Drinking Water Advisory Council established pursuant to section 1446 of the Act. At a meeting held February 26 and 27, 1975, the Council made recommendations with respect to these standards and to the extent deemed appropriate, changes have been made in view of these recommendations.

Interested persons may participate in this rulemaking process by submitting written comments in triplicate to the Water Supply Division (WH-450), Environmental Protection Agency, Washington, D.C. 20460, Attention: Comment Clerk, Interim Primary Drinking Water Standards.

Comments on all aspects of the proposed regulations are solicited. All comments received on or before May 16, 1975, will be considered. If the comments are criticisms of the adequacy of data relied upon by EPA, the comments should identify and, if possible, provide additional data from published literature and the individual should indicate why and how this information should be used.

Copies of the Statement of Basis and Purpose for these Proposed Interim Primary Standards and other relevant documents will be available after March 16, 1975, from the EPA Freedom of Information Center, Room 206, West Tower, Waterside Mall, 401 M Street, SW, Washington, D.C. 20460, Attention: Rubye Mullins. A copy of all public comments and transcripts of the public hearings will be available for inspection and copying from the EPA Freedom of Information Center. For public review and copying, the EPA Information Regulation (40 CFR Part 2) provides that a reasonable fee may be charged for the copying service.

In addition to considering public comments sent to EPA, the Agency will hold public hearings at the following locations, to receive comments and statements. Persons who wish to make statements at these sessions are urged to submit written copies of their remarks in triplicate at the time they are presented for inclusion in the record. Persons wishing to attend are also urged to confirm by telephone the exact location of the hearing.

April 15, 1975 9:30 a.m.	EPA Region I John F. Kennedy Federal Building Boston, Mass. 02203 Telephone: (617) 223-6486
April 17, 1975 9:30 a.m.	EPA Region V 230 S. Dearborn St. Chicago, Illinois Telephone: (312) 553-7736
April 22, 1975 9:30 a.m.	EPA Region IX 100 California St. San Francisco, California 94111 Telephone: (415) 556-2005
April 25, 1975 9:30 a.m.	Washington, D.C. EPA Headquarters Waterside Mall 401 M Street SW Washington, D.C. 20460 Telephone: (202) 426-8847

Dated: March 10, 1975.

RUSSELL E. TRAIN,
Administrator.

SUBCHAPTER D—WATER PROGRAMS

PART 141—NATIONAL INTERIM PRIMARY DRINKING WATER STANDARDS

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AUTHORITY: Secs. 1412, 1414, 1415, 1450 of Pub. L. 93-523.

§ 141.1 Applicability.

This subpart sets forth the interim primary drinking water standards required by section 1412 of the Safe Drinking Water Act (Pub. L. 93-523).

§ 141.2 Definitions.

As used in this subpart the term:

(a) "Act" means the Safe Drinking Water Act, Pub. L. 93-523.

(b) "Community water system" means a public water system which serves a population of which 70 percent or greater are residents.

(c) "Contaminant" means any physical, chemical, biological, or radiological substance or matter in water.

(d) "Maximum contaminant level" means the maximum permissible level of a contaminant in water which is delivered to the free flowing outlet of the ultimate user of a public water system.

(e) "Person" means an individual, corporation, company, association, partnership, State, municipality, or Federal agency.

(f) "Public water system" means a system for the provision to the public of piped water for human consumption, if such system has at least fifteen service connections or regularly serves an average of at least twenty-five individuals daily at least three months out of the year. Such term includes (1) any collection, treatment, storage, and distribution facilities under control of the operator of such system and used primarily in connection with such system, and (2) any collection or pretreatment storage facilities not under such control which are used primarily in connection with such system.

(g) "State" means the agency of the State government which has jurisdiction over public water systems. During any period when a State does not have primary enforcement responsibility, the term 'State' means the Regional Administrator, Environmental Protection Agency.

(h) "Supplier of water" means any person who owns or operates a public water system.

§ 141.3 Coverage.

The interim primary drinking water standards under this subpart shall apply to each public water system in a State, except that such standards shall not apply to a public water system which—

(a) Consists only of distribution and storage facilities (and does not have any collection and treatment facilities);

(b) Obtains all of its water from, but is not owned or operated by, a public water system to which such regulations apply;

(c) Does not sell water to any person; and

(d) Is not a carrier which conveys passengers in interstate commerce.

§ 141.11 Maximum contaminant levels for inorganic chemicals.

(a) The following are the maximum contaminant levels for inorganic chemicals:

Contaminant:	*Level (mg/l)*
Arsenic	0.05
Barium	1.
Cadmium	0.010
Chromium	0.05
Cyanide	0.2
Lead	0.05
Mercury	0.002
Nitrate (as N)	10.
Selenium	0.01
Silver	0.05

(b) When the annual average of the maximum daily air temperatures for the location in which the public water system is situated is the following, the corresponding concentration of fluoride shall not be exceeded:

Temperature (in F°)	(C°)	Level (mg/l)
50.0 to 53.7	10.0 to 12.0	2.4
53.8 to 58.3	12.1 to 14.6	2.2
58.4 to 63.8	14.7 to 17.6	2.0
63.9 to 70.6	17.7 to 21.4	1.8
70.7 to 79.2	21.5 to 26.2	1.6
79.3 to 90.5	26.3 to 32.5	1.4

The requirements of this paragraph (b) do not apply to public water supplies serving only educational institutions.

§ 141.12 Maximum contaminant levels for organic chemicals.

The maximum contaminant level for the total concentration of organic chemicals, as determined by the carbon chloroform extract method set forth in § 141.24(b), is 0.7 mg/l.

§ 141.13 Maximum contaminant levels for pesticides.

The following are the maximum contaminant levels for pesticides:

(a) Chlorinated Hydrocarbons:

	Level mg/l
Chlordane (cis and trans) (1,2,4,5,-6,7,8,8 - Octachloro - 3a,4,5,7a-tetrahydro-4,7-methanoindan)	0.003
Endrin (1,2,3,4,10,10 - Hexachloro-6,7 - epoxy - 1,4,4a,5,6,7,8,8a-octahydro-1,4-endo, endo-5,8-dimethano naphthalene)	0.0002
Heptachlor (1,4,5,6,7,8,8-Heptachloro-3a,4,7,7a-tetrahydro 4,7-methanoindene)	0.0001
Heptochlor Epoxide (1,4,5,6,7,8,8-Heptachloro - 2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindan)	0.0001
Lindane (1,2,3,4,5,6-Hexachlorocyclohexane, gamma isomer)	0.004
Methoxychlor (1,1,1-Trichloro-2,2-bis [p-methoxyphenyl] ethane)	0.1
Toxaphene ($C_{10}H_{10}Cl_8$—Technical chlorinated camphene, 67-69% chlorine)	0.005

(b) Chlorophenoxys:

2,4-D (2,4-Dichlorophenoxyacetic acid)	0.1
2,4,5-TP Silvex (2,4,5-Trichlorophenoxypropionic acid)	0.01

§ 141.14 Maximum contaminant level of turbidity.

The maximum contaminant level of turbidity in the drinking water at a representative entry point(s) to the distribution system is one turbidity unit (TU), as determined pursuant to § 141.22, except that five or fewer turbidity units may be allowed if the supplier of water can demonstrate to the State that the higher turbidity does not:

(a) Interfere with disinfection;

(b) Prevent maintenance of an effective disinfectant agent throughout the distribution system; and

(c) Interfere with microbiological determinations.

§ 141.15 Maximum microbiological contaminant levels.

(a) The supplier of water may employ one of two methods to determine compliance with the coliform maximum contaminant levels.

(1) When the supplier of water employs the membrane filter technique pursuant to § 141.21(a) the coliform densities shall not exceed one per 100 milliliters as the arithmetic mean of all samples examined per month; and either

(i) Four per 100 milliliters in more than one standard sample when less than 20 are examin[illegible] per month; or

(ii) Four per 10[illegible] milliliters in more than five percent of the standard samples when 20 or more are examined per month.

(2)(i) When the supplier of water employs the fermentation tube method and 10 milliliter standard portions pursuant to § 141.21, coliforms shall not be present in more than 10 percent of the portions in any month; and either

(A) Three or more portions in one sample when less than 20 samples are examined per month; or

(B) Three or more portions in more than five percent of the samples if 20 or more samples are examined per month.

(ii) When the supplier of water employs the fermentation tube method and 100 milliliter standard portions pursuant to § 141.21(a) coliforms shall not be present in more than 60 percent of the portions in any month; and either

(A) Five or more portions in more than one sample when less than five samples are examined; or

(B) Five or more portions in more than 20 percent of the samples when five samples or more are examined.

(b) The supplier of water shall provide water in which there shall be no greater than 500 organisms per one milliliter as determined by the standard bacterial plate count provided in § 141.21(f).

§ 141.16 Substitution of residual chlorine measurement for total coliform measurement.

(a) The supplier of water may, with the approval of the State, substitute the use of chlorine residual monitoring for not more than 75 percent of the samples required to be taken by § 141.21(b), provided that the supplier of water takes chlorine residual samples at points which are representative of the conditions within the distribution system at the frequency of at least four for each substituted microbiological sample. There shall be at least daily determinations of chlorine residual. Measurements shall be made in accordance with "Standard Methods," 13th Ed., pp 129–132. When the supplier of water exercises the option provided in this paragraph (a), he shall maintain no less than 0.2 mg/l free chlorine in the public water distribution system.

(b) For public water systems serving 4900 or fewer persons, the supplier may, with the approval of the State, make a total substitution of chlorine residual measurement for the samples required to be taken by § 141.21(b): *Provided*, That the supplier of water takes chlorine residual samples at points which are representative of the conditions within the distribution system at the rate of one per day for each microbiological sample required to be taken per month under § 141.21. When the supplier of water exercises the option provided by this paragraph (b) he shall maintain no less than 0.3 mg/l free chlorine in the public water distribution system. Measurements shall be made in accordance with "Standard Methods," 13th Ed., pp 129–132.

§ 141.21 Microbiological contaminant sampling and analytical requirements.

(a) The supplier of water shall make coliform density measurements, for the purpose of determining compliance with § 141.15, in accordance with the analytical recommendations set forth in "Standard Methods for the Examination of Water and Wastewater," American Public Health Association, 13th Edition, pp 662–688, except that only a 100 milliliter sample size shall be employed in the membrane filter technique. The samples shall be taken at points which are representative of the conditions within the distribution system.

(b) The supplier of water shall take coliform density samples at regular intervals throughout the month, and in number proportionate to the population served by the public water system. In no event shall the frequency be less than as set forth below:

Population served:	*Minimum number of samples per month*
25 to 2,500	2
2,501 to 3,300	3
3,301 to 4,100	4
4,101 to 4,900	5
4,901 to 5,800	6
5,801 to 6,700	7
6,701 to 7,600	8
7,601 to 8,500	9
8,501 to 9,400	10
9,401 to 10,300	11
10,301 to 11,100	12
11,101 to 12,000	13
12,001 to 12,900	14
12,901 to 13,700	15
13,701 to 14,600	16
14,601 to 15,500	17
15,501 to 16,300	18
16,301 to 17,200	19
17,201 to 18,100	20
18,101 to 18,900	21
18,901 to 19,800	22
19,801 to 20,700	23
20,701 to 21,500	24
21,501 to 22,300	25
22,301 to 23,200	26
23,201 to 24,000	27
24,001 to 24,900	28
24,901 to 25,000	29
25,001 to 28,000	30
28,001 to 33,000	35
33,001 to 37,000	40
37,001 to 41,000	45
41,001 to 46,000	50
46,001 to 50,000	55
50,001 to 54,000	60
54,001 to 59,000	65
59,001 to 64,000	70
64,001 to 70,000	75
70,001 to 76,000	80
76,001 to 83,000	85
83,001 to 90,000	90
90,001 to 96,000	95
96,001 to 111,000	100
111,001 to 130,000	110
130,001 to 160,000	120
160,001 to 190,000	130
190,001 to 220,000	140
220,001 to 250,000	150
250,001 to 290,000	160
290,001 to 320,000	170

Population served	*Minimum number of samples per month*
320,001 to 360,000	180
360,001 to 410,000	190
410,001 to 450,000	200
450,001 to 500,000	210
500,001 to 550,000	220
550,001 to 600,000	230
600,001 to 660,000	240
660,001 to 720,000	250
720,001 to 780,000	260
780,000 to 840,000	270
840,001 to 910,000	280
910,001 to 970,000	290
970,001 to 1,050,000	300
1,050,001 to 1,140,000	310
1,140,001 to 1,230,000	320
1,230,001 to 1,320,000	330
1,320,001 to 1,420,000	340
1,420,001 to 1,520,000	350
1,520,001 to 1,630,000	360
1,630,001 to 1,730,000	370
1,730,001 to 1,850,000	380
1,850,001 to 1,970,000	390
1,970,001 to 2,060,000	400
2,060,001 to 2,270,000	410
2,270,001 to 2,510,000	420
2,510,001 to 2,750,000	430
2,750,001 to 3,020,000	440
3,020,001 to 3,320,000	450
3,320,001 to 3,620,000	460
3,620,001 to 3,960,000	470
3,960,001 to 4,310,000	480
4,310,001 to 4,690,000	490
>4,690,000	500

(c) (1) When the coliform colonies in a single standard sample exceed four per 100 milliliters (§ 141.15(a)(1)), daily samples shall be collected and examined from the same sampling point until the results obtained from at least two consecutive samples show less than one coliform per 100 milliliters.

(2) When organisms of the coliform group occur in three or more 10 ml portions of a single standard sample (§ 141.15(a)(2)(i)), daily samples shall be collected and examined from the same sampling point until the results obtained from at least two consecutive samples show no positive tubes.

(3) When organisms of the coliform group occur in all five of the 100 ml portions of a single standard sample (§ 141.15(a)(2)(ii)), daily samples shall be collected and examined from the same sampling point until the results obtained from at least two consecutive samples show no positive tubes.

(4) The location at which the check sample was taken pursuant to paragraphs (c) (1), (2) or (3) of this section must not be eliminated from future sampling because of a history of questionable water quality. Check samples shall not be included in calculating the total number of samples taken each month to determine compliance with § 141.15.

(d) When a particular sampling point has been confirmed, by the first check sample examined as directed in paragraphs (c) (1), (2), or (3) of this section, to be in non-compliance with the maximum contaminant levels set forth in § 141.15, the supplier of water shall notify the State as prescribed in § 141.31.

(e) When the maximum contaminant levels set forth in paragraphs (a) (1) or (2) of § 141.15 are exceeded as confirmed by check samples taken pursuant to paragraphs (c) (1), (2), or (3) of this section, the supplier of water shall report as directed in § 141.32(a).

(f) When a particular sampling point has been shown to be in non-compliance with the requirements of § 141.16, water from that location shall be retested within one hour. If the non-compliance is confirmed, the State shall be notified as prescribed in § 141.31. Also, if the non-compliance is confirmed, a sample for coliform analysis must be immediately collected from that sampling point and the results of such analysis reported to the State.

(g) Standard bacteria plate count samples shall be analyzed in accordance with the recommendation set forth in "Standard Methods for the Examination of Water and Wastewater," American Public Health Association, 13th Edition, pp 660–662. Samples taken for the purpose of plate count analysis shall be collected at points which are representative of conditions within the distribution system at a frequency at least equal to 10 percent of the frequency for coliform analysis as directed in paragraph (b) of this section with the exception that at least one sample shall be collected and analyzed monthly.

§ 141.22 Turbidity sampling and analytical requirements.

(a) Samples shall be taken at a representative entry point(s) to the water distribution system at least once per day (at least once per month for supplies using water obtained from underground sources) for the purpose of making turbidity measurements to determine compliance with § 141.14. The measurement shall be made in accordance with the recommendations set forth in "Standard Methods for the Examination of Water and Wastewater," American Public Health Association, 13th Edition, pp. 350–353 (Nephelometric Method).

(b) In the event that such measurement indicates that the maximum allowable limit has been exceeded, the sampling and measurement shall be repeated within one hour. The results of the two measurements shall be averaged, and if the average confirms that the maximum allowable limit has been exceeded, this average shall be reported as directed in § 141.31. If the monthly average of all samples exceeds the maximum allowable limit, this fact shall be reported as directed in § 141.32(a).

(c) The requirements of this § 141.22 shall not apply to public water systems other than community water systems which use water obtained from underground sources.

§ 141.23 Inorganic chemical sampling and analytical requirements.

(a)(1) To establish an initial record of water quality, an analysis of substances for the purpose of determining compliance with § 141.111 shall be completed for all community water systems utilizing surface water sources within one year following the effective date of this subpart. This analysis shall be repeated at yearly intervals.

(2) An analysis for communtiy water systems utilizing ground water sources shall be completed within two years following the effective date of this subpart. This analysis shall be repeated at three-year intervals.

(3) Analyses for public water systems other than community water systems, whether supplied by surface or ground water sources, shall be completed within six years following the effective date of this subpart. These analyses shall be repeated at five-year intervals.

(b) If the supplier of water determines or has been informed by the State that the level of any contaminant is 75 percent or more of the maximum contaminant level, he shall analyze for the presence and quantity of that contaminant at least once per month following the initial analysis or information. If, after conducting monthly testing for a period of at least one year, the supplier of water demonstrates to the satisfaction of the State that the level of such contaminant is stable and due to a natural condition of the water source, he may reduce the frequency of analysis for that contaminant consistent with the requirements of paragraph (a) of this section.

(c) If the supplier of water determines or has been informed by the State that the level of any contaminant listed in § 141.11 exceeds the maximum contaminant level for the substance, he shall confirm such determination or information by repeating the analysis within 24 hours following the initial analysis or information, and then at least at weekly intervals during the period of time the maximum contaminant level for that substance has been exceeded, or until a monitoring schedule as a condition to a variance, exemption or enforcement action shall become effective. The results of such repetitive testing shall be averaged and reported as prescribed in paragraph (d) of this section.

(d) To judge the compliance of a public water system with the maximum contaminant levels listed in § 141.11, averages of data shall be used and shall be rounded to the same number of significant figures as the maximum contaminant level for the substance in question. Each average shall be calculated on a past 12-month moving average basis if less than twelve samples per year are analyzed, and on a past three month moving average basis if twelve or more samples per year are analyzed. In cases where the maximum contaminant level has been exceeded in any one sample, the average concentration shall be calculated on a one-month moving average basis and reported pursuant to § 141.31. If the mean of the samples comprising the one month moving average exceeds the maximum contaminant level, the supplier of water shall give public notice pursuant to § 141.32(a).

(e) The provisions of paragraphs (c) and (d) of this section notwithstanding, compliance with the maximum contaminant level for nitrate shall be determined on the basis of individual analyses rather than by averages. When a level exceeding the maximum contaminant level for nitrate is found, the analyses shall be repeated within 24 hours, and if the mean of the two analyses exceeds the maximum contaminant level, the supplier of water shall report his findings pursuant to §§ 141.31 and 141.32(a).

(f) Analyses conducted to determine compliance with § 141.11 shall be made in accordance with the following methods:

(1) Arsenic—Atomic Absorption Method, "Methods for Chemical Analysis of Water and Wastes," pp. 95–96, Environmental Protection Agency, Office of Technology Transfer, Washington, D.C. 20460, 1974.

(2) Barium—Atomic Absorption Method, "Standard Methods for the Examination of Water and Wastewater," 13th Edition, pp. 210–215, or "Methods for Chemical Analysis of Water and Wastes," pp. 97–98, Environmental Protection Agency, Office of Technology Transfer, Washington, D.C. 20460, 1974.

(3) Cadmium—Atomic Absorption Method, "Standard Methods for the Examination of Water and Wastewater," 13th Edition, pp. 210–215, or "Methods for Chemical Analysis of Water and Wastes," pp. 101–103, Environmental Protection Agency, Office of Technology Transfer, Washington, D.C. 20460, 1974.

(4) Chromium—Atomic Absorption Method, "Standard Methods for the Examination of water and Wastewater," 13th Edition, pp. 210–215, or "Methods for Chemical Analysis of Water and Wastes," pp. 105–106, Environmental Protection Agency, Office of Technology Transfer, Washington, D.C. 20460, 1974.

(5) Cyanide—Titration or Colorimetric Methods, "Methods for Chemical Analysis of Water and Wastes," pp. 40–48, Environmental Protection Agency, Office of Technology Transfer, Washington, D.C. 20460, 1974.

(6) Lead—Atomic Absorption Method, "Standards Methods for the Examination of Water and Wastewater," 13th Edition, pp. 210–215, or "Methods for Chemical Analysis of Water and Wastes," pp. 112–113, Environmental Protection Agency, Office of Technology Transfer, Washington, D.C. 20460, 1974.

(7) Mercury—Flameless Atomic Absorption Method, "Methods for Chemical Analysis of Water and Wastes," pp. 118–126, Environmental Protection Agency, Office of Technology Transfer, Washington, D.C. 20460, 1974.

(8) Nitrate—Brucine Colorimetric Method, "Standard Methods for the Examination of Water and Wastewater," 13th Edition, pp. 461–464, or Cadmium Reduction Method, "Methods for Chemical Analysis of Water and Wastes," pp. 201–206, Environmental Protection Agency, Office of Technology Transfer, Washington, D.C. 20460, 1974.

(9) Selenium—Atomic Absorption Method, "Methods for Chemical Analysis of Water and Wastes," p. 145, Environmental Protection Agency, Office of Technology Transfer, Washington, D.C. 20460, 1974.

(10) Silver—Atomic Absorption Method, "Standard Methods for the Examination of Water and Wastewater," 13th Edition, pp. 210–215, or "Methods for Chemical Analysis of Water and Wastes," p. 146, Environmental Protection Agency, Office of Technology Transfer, Washington, D.C. 20460, 1974.

(11) Fluoride—Electrode Method, "Standard Methods for the Examination of Water and Wastewater," 13th Edition, pp. 172–174, or "Methods for Chemical Analysis of Water and Wastes," pp. 65–67, Environmental Protection Agency, Office of Technology Transfer, Washington, D.C. 20460, 1974, or Colorimetric Method with Preliminary Distillation, "Standard Methods for the Examination of Water and Wastewater," 13th Edition, pp. 171–172 and 174–176, or "Methods for Chemical Analysis of Water and Wastes," pp. 59–60, Environmental Protection Agency, Office of Technology Transfer, Washington, D.C. 20460, 1974.

§ 141.24 Pesticide and organic chemicals sampling and analytical requirements.

(a)(1) To establish an initial record of water quality, an analysis of substances for the purpose of determining compliance with §§ 141.12 and 141.13 shall be completed for all community water systems utilizing surface water sources within one year following the effective date of this subpart. This analysis shall be repeated at yearly intervals.

(2) An analysis for community water systems utilizing ground water sources shall be completed within two years following the effective date of this subpart. This analysis shall be repeated at three-year intervals.

(3) Analyses for public water systems other than community water systems, whether supplied by surface or ground water sources, shall be completed within six years following the effective date of this subpart. These analyses shall be repeated at five-year intervals.

(b) If the supplier of water determines or has been informed by the State that the level of any contaminant is 75 percent or more of the maximum contaminant level, he shall analyze for the presence and quantity of that contaminant at least once per month following the initial analysis or information. If, after conducting monthly testing for a period of at least one year, the supplier of water demonstrates to the satisfaction of the State that the level of such contaminant is stable and due to a natural condition of the water source, he may reduce the frequency of analysis for that contaminant consistent with the requirements of paragraph (a) of this section.

(c) If the supplier of water determines or has been informed by the State that the level of contaminants set forth in § 141.12 exceeds the maximum contaminant level, he shall confirm such determination or information by repeating the analyses within two weeks following the initial analysis or information. The average of the two analyses, if in excess of the maximum contaminant level, shall be reported as directed in §§ 141.31 and 141.32(a).

(d) If the supplier of water determines or has been informed by the State that the level of any contaminant listed in § 141.13 exceeds the maximum contaminant level for the substance, he shall confirm such determination or information by repeating the analysis within 24 hours following the initial analysis or information, and then at least at weekly intervals during the period of time the maximum contaminant level for that substance has been exceeded, or until a monitoring schedule as a condition to variance, exemption or enforcement action shall become effective. The results of such repetitive testing shall be averaged and reported as prescribed in paragraph (e) of this section.

(e) To judge the compliance of a public water system with the maximum contaminant levels listed in § 141.13, averages of data shall be used and shall be rounded to the same number of significant figures as the maximum contaminant level for the substance in question. Each average shall be calculated on a past 12-month moving average basis if less than twelve samples per year are analysed, and on a past three month moving average basis if twelve or more samples per year are analysed. In cases where the maximum contaminant levels of § 141.13 have been exceeded in any one sample, the average concentration shall be calculated on a one-month moving average basis and reported pursuant to § 141.31. If the mean of the samples comprising the one month moving average exceeds the maximum contaminant level, the supplier of water shall give public notice pursuant to § 141.32(a).

(f) Sampling and analyses made to determine compliance with § 141.12 shall be made in accordance with "An Improved Method for Determining Organics in Water by Activated Carbon Absorption and Solvent Extraction," Parts 1 and 2, Buelow, et al., Journal of American Water Works Association, 65: 57, 197 (1973).

(g) Analyses made to determine compliance with § 141.13(a) shall be made in accordance with "Method for Organochlorine Pesticides in Industrial Effluents," MDQARL, Environmental Protection Agency, Cincinnati, Ohio, November 28, 1973.

(h) Analyses made to determine compliance with § 141.13(b) shall be conducted in accordance with "Methods for Chlorinated Phenoxy Acid Herbicides in Industrial Effluents," MDQARL, Cincinnati, Ohio, November 23, 1973.

§ 141.27 Laboratory certification.

For the purposes of determining compliance with §§ 141.21 through 141.24, samples may be considered only if they have been analyzed by a laboratory approved by the State. The approval shall be contingent upon maintenance of proper laboratory methods and technical competence and upon the retention for inspection at reasonable times of analytical results. Approved laboratories shall make periodic reports as required by the State.

§ 141.31 Reporting requirements.

The supplier of water shall report within 40 days following a test, measurement or analysis required to be made by this subpart, the results of that test, measurement or analysis: *Provided*, That the supplier of water shall report within 36 hours the failure to meet any standards (including failure to comply with monitoring requirements) set forth in this subpart. Reports required to be made by this § 141.31 shall be communicated to the State, except that Federal Agencies shall report to the Regional Administrator.

§ 141.32 Public notification of variances, exemptions and noncompliance with standards.

(a) The supplier of water shall give notice to the persons served by the public water system of any failure on the part of the system to comply with the requirements (including monitoring requirements) of this subpart. The supplier of water shall give the notice required by this § 141.32 not less than once every three months during the life of the noncompliance:

(1) By publication on not less than three consecutive days in a newspaper or newspapers of general circulation serving the area served by such public water system, which newspaper or newspapers shall be approved by the State. With respect to the public water systems operated by Federal Agencies, the newspapers cited in this paragraph shall be approved by the Regional Administrator;

(2) By furnishing a copy thereof to the radio and television stations serving such area as soon as practicable but not later than 36 hours after confirmation of the noncompliance with respect to which the notice is required; and

(3) By inclusion with the water bills of the public water system at least once every three months if the water bills are issued at least once every three months, and with every water bill if they are issued less often. If water bills are not issued, other means of notification acceptable to the State may be used. The notice required by this § 141.32 shall state at least that the public water system fails to monitor, operate the system or provide water which meets all the requirements of this subpart and shall state with particularity those requirements for which there is noncompliance. If a quantitive limitation has been exceeded, the notice shall state what the Federal or State limitation is, and at what level of performance the water supply system has been operating.

(b) The supplier of water shall give notice pursuant to the procedures set forth in paragraph (a) of this section—

(1) When his system has received a variance under section 1415(a)(1) or 1415(a)(2) of the Act, and shall continue the notification process at no less than three month intervals during the life of the variance;

(2) When his system has received an exemption under section 1416 and shall continue the notification process at no less than three month intervals during the life of the exemption; or

(3) When his system has failed to comply with any schedule or control measure prescribed pursuant to a variance or exemption and shall continue the notification process at no less than the three month intervals during the life of the variance and exemption.

§ 141.41 Siting requirements.

Before a person may enter into a financial commitment for or initiate construction of a new public water system or increase the capacity of an existing public water system, he shall—

(a) To the extent practicable, avoid locating part or all of the new or expanded facility at a site which:

(1) Is subject to earthquakes, floods, fires or other man-made disasters which could cause breakdown of the public water system or a portion thereof; and

(2) Is within the floodplain of a 100 year flood;

(b) Notify the State.

§ 141.51 Effective date.

The standards set forth in this subpart shall take effect 18 months after the date of promulgation.

[FR Doc.75-6603 Filed 3-13-75;8:45 am]

APPENDIX D

(Reproduced from Federal Register, Vol. 38, No. 199, October 16, 1973, Page 28758).

Title 40—Protection of Environment

CHAPTER I—ENVIRONMENTAL PROTECTION AGENCY

SUBCHAPTER D—WATER PROGRAMS

PART 136—GUIDELINES ESTABLISHING TEST PROCEDURES FOR THE ANALYSIS OF POLLUTANTS

Notice was pubished in the FEDERAL REGISTER issue of June 29, 1973 (38 FR 17318) at 40 CFR 130, that the Environmental Protection Agency (EPA) was giving consideration to the testing procedures required pursuant to section 304(g) of the Federal Water Pollution Control Act Amendments of 1972 (86 Stat. 816, et seq., Pub. L. 92–500 (1972)) hereinafter referred to as the Act. These considerations were given in the form of proposed guidelines establishing test procedures.

Section 304(g) of the Act requires that the Administrator shall promulgate guidelines establishing test procedures for the analysis of pollutants that shall include factors which must be provided in: 1, any certification pursuant to section 401 of the Act, or 2, any permit application pursuant to section 402 of the Act. Such test procedures are to be used by permit applicants to demonstrate that effluent discharges meet applicable pollutant discharge limitations, and by the States and other enforcement activities in routine or random monitoring of effluents to verify effectiveness of pollution control measures.

These guidelines require that discharge measurements, including but not limited to the pollutants and parameters listed in Table I, be performed by the test procedures indicated; or under certain circumstances by other test procedures for analysis that may be more advantageous to use, when such other test procedures have the approval of the Regional Administrator of the Region where such discharge will occur, and when the Director of an approved State National Pollutant Discharge Elimination System (NPDES) Program (hereinafter referred to as the Director) for the State in which such discharge will occur has no objection to such approval.

The list of test procedures in Table I is published herein as final rulemaking and represents major departures from the list of proposed test procedures which was published in 38 FR 17318, dated June 29, 1973. These revisions were made after carefully considering all written comments which were received pertaining to the proposed test procedures. All written comments are on file and available for public review with the Quality Assurance Division, Office of Research and Development, EPA, Washington, D.C.

The principal revisions to the proposed test procedures are as follows:

1. Where several reliable test procedures for analysis are available from the given references for a given pollutant or parameter, each such test procedure has been approved for use for making the measurements required by sections 401 and 402 and related sections of the Act. Approved test procedures have been selected to assure an acceptable level of intercomparability of pollutants discharge data. For several pollutants and parameters it has still been necessary to approve only a single test procedure to assure this level of acceptability. This is a major departure from the proposed test procedures which would have required the use of a single reference method for each pollutant or parameter.

2. Under certain circumstances a test procedure not shown on the approved list may be considered by an applicant to be more advantageous to use. Under guidelines in §§ 136.4 and 136.5 it may be approved by the Regional Administrator of the Region where the discharge will occur, providing the Director has no objections. Inasmuch as there is no longer a single approved reference method against which a comparison can be made, the procedures for establishing such comparisons that were required by the proposed test procedures in § 130.4(b) have been deleted from this final guideline for test procedures for the analysis of pollutants.

3. A mechanism is also provided to assure national uniformity of such approvals of alternate test procedures for the analysis of pollutants. This is achieved through a centralized, internal review within the EPA of all applications for the use of alternate testing procedures. These will be reviewed and approved or disapproved on the basis of submitted information and other available information and laboratory tests which may be required by the Regional Administrator.

As deemed necessary, the Administrator will expend or revise these guidelines to provide the most responsive and appropriate list of test procedures to meet the requirements of sections 304(g), 401 and 402 of the Act, as amended.

These final guidelines establishing test procedures for the analysis of pollutants supersede the interim list of test procedures published in the FEDERAL REGISTER on April 19, 1973 (38 FR 9740) at 40 CFR Part 126 and subsequent procedures published on July 24, 1973 (38 FR 19894) at 40 CFR Part 124. Those regulations established interim test procedures for the submittal of applications under section 402 of the Act. Because of the importance of these guidelines for test procedures for the analysis of pollutants to the National Pollution Discharge Elimination System (NPDES), the Administrator finds good cause to declare that these guidelines shall be effective October 16, 1973.

JOHN QUARLES,
Acting Administrator.

OCTOBER 3, 1973.

PART 136—TEST PROCEDURES FOR THE ANALYSIS OF POLLUTANTS

Sec.
136.1 Applicability.
136.2 Definitions.
136.3 Identification of test procedures.
136.4 Application for alternate test procedures.
136.5 Approval of alternate test procedures.

AUTHORITY: Sec. 304(g) of Federal Water Pollution Control Act Amendments of 1972 86 Stat. 816, et seq., Pub. L. 92–500).

§ 136.1 Applicability.

The procedures prescribed herein shall, except as noted in § 136.5, be used to perform the measurements indicated whenever the waste constituent specified is required to be measured for:

(a) An application submitted to the Administrator, or to a State having an approved NPDES program, for a permit under section 402 of the Federal Water Pollution Control Act as amended (FWPCA), and,

(b) Reports required to be submitted by dischargers under the NPDES established by Parts 124 and 125 of this chapter, and,

(c) Certifications issued by States pursuant to section 401 of the FWPCA, as amended.

§ 136.2 Definitions.

As used in this part, the term:

(a) "Act" means the Federal Water Pollution Control Act, as amended, 33 U.S.C. 1314, et seq.

(b) "Administrator" means the Administrator of the U.S. Environmental Protection Agency.

(c) "Regional Administrator" means one of the EPA Regional Administrators.

(d) "Director" means the Director of the State Agency authorized to carry out an approved National Pollutant Discharge Elimination System Program under section 402 of the Act.

(e) "National Pollutant Discharge Elimination System (NPDES)" means the national system for the issuance of permits under section 402 of the Act and includes any State or interstate program which has been approved by the Administrator, in whole or in part, pursuant to section 402 of the Act.

(f) "Standard Methods" means *Standard Methods for the Examination of Water and Waste Water*, 13th Edition, 1971. This publication is available from the American Public Health Association, 1015 18th St. NW., Washington, D.C. 20036.

(g) "ASTM" means *Annual Book of Standards, Part 23, Water, Atmospheric Analysis, 1972*. This publication is available from the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pennsylvania 19103.

(h) "EPA Methods" means *Methods for Chemical Analysis of Water and Wastes*, 1971, Environmental Protection Agency, Analytical Quality Control Laboratory, Cincinnati, Ohio. This publication is available from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402 (Stock Number 5501–0067).

§ 136.3 Identification of test procedures.

Every parameter or pollutant for which an effluent limitation is now specified pursuant to sections 401 and 402 of the Act is named together with test descriptions and references in Table I. The discharge parameter values for which reports are required must be determined by one of the standard analytical methods cited and described in Table I, or under certain circumstances by other methods that may be more advantageous to use when such other methods have been previously approved by the Regional Administrator of the Region in which the discharge will occur, and providing that the Director of the State in which such discharge will occur does not object to the use of such alternate test procedures.

Under certain circumstances the Regional Administrator or the Director in the Region or State where the discharge will occur may determine for a particular discharge that additional parameters or pollutants must be reported. Under such circumstances, additional test procedures for analysis of pollutants may be specified by the Regional Administrator or Director upon the recommendation of the Director of the Methods Development and Quality Assurance Research Laboratory.

TABLE I—LIST OF APPROVED TEST PROCEDURES

Parameter and units	Method	References		
		Standard methods	ASTM	EPA methods
General analytical methods:				
1. Alkalinity as CaCO $_3$mg CaCO^3/liter.	Titration: electrometric, manual or automated method—methyl orange.	p. 370	p. 148	p. 6. p. 8.
2. B.O.D. five day mg/liter.	Modified winkler or probe method	p. 489		
3. Chemical oxygen demand (C.O.D.) mg/liter.	Dichromate reflux	p. 495	p. 219	p. 17.
4. Total solids mg/liter	Gravimetric 103-105° C	p. 535		p. 280.
5. Total dissolved (filterable) solids mg/liter.	Glass fiber filtration 180° C			p. 275.
6. Total suspended (nonfilterable) solids mg/liter.	Glass fiber filtration 103-105° C	p. 537		p. 278.
7. Total volatile solids mg/liter.	Gravimetric 550° C	p. 536		p. 282.
8. Ammonia (as N) mg/liter.	Distillation—nesslerization or titration automated phenolate.			p. 134. p. 141.
9. Kjeldahl nitrogen (as N) mg/liter.	Digestion + distillation—nesslerization or titration utomated digestion phenolate.	p. 469		p. 149. p. 157.
10. Nitrate (as N) mg/liter.	Cadmium reduction; brucine sulfate; automated cadmium or hydrazine reduction.	p. 458 p. 461	p. 124	p. 170. p. 175. p. 185.
11. Total phosphorus (as P) mg/liter.	Persulfate digestion and single reagent (ascorbic acid), or manual digestion, and automated single reagent or stannous chloride.	p. 526 p. 532	p. 42	p. 235. p. 246. p. 259.
12. Acidity mg $CaCO_3$/liter	Electrometric end point or phenolphthalein end point.		p. 148	
13. Total organic carbon (TOC) mg/liter.	Combustion—infrared method [1]	p. 257	p. 702	p. 2[illegible]1.
14. Hardness—total mg $CaCO_3$/liter.	EDTA titration; automated colorimetric atomic absorption.	p. 179	p. 170	p. 76. p. 78.
15. Nitrite (as N) mg/liter.	Manual or automated colorimetric diazotisation.			p. 185. p. 195.
Analytical methods for trace metals:				
16. Aluminum—total [3] mg/liter.	Atomic absorption	p. 210		p. 98.
17. Antimony—total [3] mg/liter.	Atomic absorption [4]			
18. Arsenic—total mg/liter.	Digestion plus silver diethyldithiocarbamate; atomic absorption.[3]	p. 65 p. 62		p. 13.
19. Barium—total [3] mg/liter.	Atomic absorption [4]	p. 210		
20. Beryllium—total [3] mg/liter.	Aluminon; atomic absorption	p. 67 p. 210		
21. Boron—total mg/liter	Curcumin	p. 69		
22. Cadmium—total [3] mg/liter.	Atomic absorption; colorimetric	p. 210 p. 422	p. 692	p. 101.
23. Calcium—total [3] mg/liter.	EDTA titration; atomic absorption	p. 84	p. 692	p. 102.
24. Chromium VI mg/liter.	Extraction and atomic absorption; colorimetric.	p. 429		p. 94.
25. Chromium—total [3] mg/liter.	Atomic absorption; colorimetric	p. 210 p. 426	p. 692 p. 403	p. 104.
26. Cobalt—total [3] mg/liter.	Atomic absorption [4]		p. 692	
27. Copper—total [3] mg/liter.	Atomic absorption; colorimetric	p. 210 p. 430	p. 692 p. 410	p. 106.
28. Iron—total [3] mg/liter	do	p. 210 p. 433	p. 692 p. 152	p. 108.
29. Lead—total [3] mg/liter	do	p. 210 p. 436	p. 692	p. 110.
30. Magnesium—total [3] mg/liter.	Atomic absorption; Gravimetric	p. 210 p. 416 p. 201	p. 692	p. 112.
31. Manganese—total [3] mg/liter.	Atomic absorption	p. 210	p. 692	p. 114.
32. Mercury—total mg/liter.	Flameless atomic absorption [5]			
33. Molybdenum—total [3] mg/liter.	Atomic absorption [4]			
34. Nickel—total [3] mg/liter.	Atomic absorption; colorimetric [4]	p. 443	p. 692	
35. Potassium—total [3] mg/liter.	Atomic absorption; colorimetric; flame photometric.	p. 283 p. 285	p. 326	p. 115.
36. Selenium—total mg/liter.	Atomic absorption [3]			
37. Silver—total [3]	Atomic absorption [4]	p. 210		
38. Sodium—total [3] mg/liter.	Flame photometric; atomic absorption	p. 317	p. 326	p. 118.
39. Thallium—total [3] mg/liter.	Atomic absorption [4]			
40. Tin—total [3] mg/liter	do			
41. Titanium—total mg/liter.	do			
42. Vanadium—total [3] mg/liter.	Atomic Absorption; [4] Colorimetric	p. 157		
43. Zinc—total [3] mg/liter	Atomic Absorption; Colorimetric	p. 210 p. 444	p. 692	p. 120.
Analytical methods for nutrients, anions, and organics:				
44. Organic nitrogen (as N) mg/liter.	Kjeldahl nitrogen minus ammonia nitrogen.	p. 468		p. 149.
45. Ortho-phosphate (as P) mg/liter.	Direct single reagent; automated single reagent or stannous chloride.	p. 532	p. 42	p. 235. p. 246. p. 259.
46. Sulfate (as SO_4) mg/liter.	Gravimetric; turbidimetric; automated colorimetric—barium chloranilate.	p. 331 p. 334	p. 51 p. 52	p. 286. p. 288.
47. Sulfide (as S) mg/liter	Titrimetric—iodine	p. 551		p. 294.
48. Sulfite (as SO_3) mg/liter.	Titrimetric; iodide-iodate	p. 337	p. 261	
49. Bromide mg/liter	do		p. 216	
50. Chloride mg/liter	Silver nitrate; mercuric nitrate; automated colorimetric-ferricyanide.	p. 96 p. 97	p. 23 p. 21	p. 29. p. 31.
51. Cyanide—total mg/liter.	Distillation—silver nitrate titration or pyridine pyrazolone colorimetric.	p. 397	p. 556	p. 41.
52. Fluoride mg/liter	Distillation—SPADNS	p. 171 p. 174	p. 191	p. 64.
53. Chlorine—total residual mg/liter.	Colorimetric; amperometric titration	p. 382	p. 223	
54. Oil and grease mg/liter	Liquid-Liquid extraction with trichloro-trifluoroethane.	p. 254		
55. Phenols mg/liter	Colorimetric, 4 AAP	p. 502	p. 445	p. 232.
56. Surfactants mg/liter	Methylene blue colorimetric	p. 339	p. 619	p. 131.
57. Algicides mg/liter	Gas chromatography [6]			
58. Benzidine mg/liter	Diazotization—colorimetric [7]			
59. Chlorinated organic compounds (except pesticides) mg/liter.	Gas chromatography [6]			
60. Pesticides mg/liter	Gas chromatography [6]			
Analytical methods for physical and biological parameters:				
61. Color platinum-cobalt units or dominant wave-length, hue, luminance, purity.	Colorimetric; spectrophotometric	p. 160 p. 392		p. 36.
62. Specific conductance mho/cm at 25° C.	Wheatstone bridge	p. 323	p. 163	p. 284.
63. Turbidity jackson units.	Turbidimeter	p. 350	p. 467	p. 308.

See Note at end of Table I

Parameter and units	Method	References		
		Standard methods	ASTM	EPA methods
64. Fecal streptococci bacteria number/100 ml.	MPN; membrane filter; plate count	p. 689 p. 690 p. 691		
65. Coliform bacteria (fecal) number/100 ml.	MPN: Membrane filter	p. 669 p. 684		
66. Coliform bacteria (total) number/100 ml.	do	p. 664 p. 679		
Radiological parameters:				
67. Alpha—total pCi/liter	Proportional counter; scintillation counter	p. 598	p. 509	
68. Alpha—counting error pCi/liter.	do	p. 598	p. 512	
69. Beta—total pCi/liter	Proportional counter†	p. 598	p. 478	
70. Beta—counting error pCi/liter.	do	p. 598	p. 478	
71. Radium—total pCi/liter.	Proportional counter; scintillation counter	p. 611 p. 617	p. 674	

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[1] A number of such systems manufactured by various companies are considered to be comparable in their performance. In addition, another technique, based on Combustion-Methane Detection, is also acceptable.

[2] For the determination of total metals the sample is not filtered before processing. Choose a volume of sample appropriate for the expected level of metals. If much suspended material is present, as little as 50-100 ml of well-mixed sample will most probably be sufficient. (The sample volume required may also vary proportionally with the number of metals to be determined.)

Transfer a representative aliquot of the well-mixed sample to a Griffin beaker and add 3 ml of concentrated distilled HNO_3. Place the beaker on a hotplate and evaporate to dryness making certain that the sample does not boil. Cool the beaker and add another 3 ml portion of distilled concentrated HNO_3. Cover the beaker with a watch glass and return to the hotplate. Increase the temperature of the hotplate so that a gentle reflux action occurs. Continue heating, adding additional acid as necessary until the digestion is complete, generally indicated by a light colored residue. Add (1:1 with distilled water) distilled concentrated HCl in an amount sufficient to dissolve the residue upon warming. Wash down the beaker walls and the watch glass with distilled water and filter the sample to remove silicates and other insoluble material that could clog the atomizer. Adjust the volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis. Concentrations so determined shall be reported as "total".

[3] See D. C. Manning, "Technical Notes", Atomic Absorption Newsletter, Vol. 10, No. 6 p. 123, 1971. Available from Perkin-Elmer Corporation, Main Avenue, Norwalk, Connecticut 06852.

[4] Atomic absorption method available from Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, USEPA, Cincinnati, Ohio 45268.

[5] For updated method, see: Journal of the American Water Works Association 64, No. 1, pp. 20-25 (Jan. 1972) or ASTM Method D 3223-73, American Society for Testing and Materials Headquarters, 1916 Race St., Philadelphia, Pa. 19103.

[6] Interim procedures for algicides, chlorinated organic compounds, and pesticides can be obtained from the Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, USEPA, Cincinnati, Ohio 45268.

[7] Benzidine may be estimated by the method of M.A. El-Dib, "Colorimetric Determination of Aniline Derivatives in Natural Waters", El-Dib, M.A., Journal of the Association of Official Analytical Chemists, Vol. 54, No. 6, Nov., 1971, pp. 1383-1387.

†As a prescreening measurement.

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§ 136.4 Application for alternate test procedures.

(a) Any person may apply to the Regional Administrator in the Region where the discharge occurs for approval of an alternative test procedure.

(b) When the discharge for which an alternative test procedure is proposed occurs within a State having a permit program approved pursuant to section 402 of the Act, the applicant shall submit his application to the Regional Administrator through the Director of the State agency having responsibility for issuance of NPDES permits within such State.

(c) Unless and until printed application forms are made available, an application for an alternate test procedure may be made by letter in triplicate. Any application for an alternate test procedure under this subchapter shall:

(1) Provide the name and address of the responsible person or firm making the discharge (if not the applicant) and the applicable ID number of the existing or pending permit, issuing agency, and type of permit for which the alternate test procedure is requested, and the discharge serial number.

(2) Identify the pollutant or parameter for which approval of an alternate testing procedure is being requested.

(3) Provide justification for using testing procedures other than those specified in Table I.

(4) Provide a detailed description of the proposed alternate test procedure, together with references to published studies of the applicability of the alternate test procedure to the effluents in question.

§ 136.5 Approval of alternate test procedures.

(a) The Regional Administrator of the region in which the discharge will occur has final responsibility for approval of any alternate test procedure.

(b) Within thirty days of receipt of an application, the Director will forward such application, together with his recommendations, to the Regional Administrator. Where the Director recommends rejection of the application for scientific and technical reasons which he provides, the Regional Administrator shall deny the application, and shall forward a copy of the rejected application and his decision to the Director of the State Permit Program and to the Director of the Methods Development and Quality Assurance Research Laboratory.

(c) Before approving any application for an alternate test procedure, the Regional Administrator shall forward a copy of the application to the Director of the Methods Development and Quality Assurance Laboratory for review and recommendation.

(d) Within ninety days of receipt by the Regional Administrator of an application for an alternate test procedure, the Regional Administrator shall notify the applicant and the appropriate State agency of approval or rejection, or shall specify the additional information which is required to determine whether to approve the proposed test procedure. Prior to the expiration of such ninety day period, a recommendation providing the scientific and other technical basis for acceptance or rejection will be forwarded to the Regional Administrator by the Director of the Methods Development and Quality Assurance Research Laboratory. A copy of all approval and rejection notifications will be forwarded to the Director, Methods Development and Quality Assurance Research Laboratory, for the purposes of national coordination.

[FR Doc.73-21466 Filed 10-15-73;8:45 am]

K. EXPLANATION OF INSTRUMENT NOTES

In the following sections are the Instrument Notes for those instruments either commercially available or expected to become so shortly. For each group of pollutants or parameters, e.g. Metals, the notes are divided into two sections: Field Monitors (for water-monitoring at streams, reservoirs, estuaries, etc.) and Laboratory Monitors. The descriptor in the upper right-hand corner identifies the type of use. Some instruments fall into both types of use. The notes are arranged alphabetically by manufacturer and each model has been assigned a number. The reader is referred to the Indexing Method for an understanding of descriptors in the upper right-hand corner of the notes, and to the Glossary for an understanding of the terms used in the Instrument Notes. The Table of Instruments in each group summarizes the information contained in the Instrument Notes and may serve as a preliminary guide.

The manufacturer's specifications are shown if available, and we gratefully acknowledge those manufacturers who have assisted in the compilation of their notes. Specifications and comments reported by independent workers are also shown and are footnoted and referenced. All information not footnoted has been supplied by the manufacturer, either from brochures and manuals or by private communication. If no information is given for a particular specification for an instrument, there is none available.

The Instrument Notes should not be used as separate entities in themselves. The reader should first refer to the discussion sections preceding the Instrument Notes.

The technical information in these notes have been compiled from the best available sources and is believed to be correct and up-to-date. These notes will be continually updated, and additional information and comments are certainly solicited.

CALIBRATION OF WATER MONITORING INSTRUMENTATION

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A. INTRODUCTION

1. Purpose of Calibration

The increasing recognition after the Second World War that the water resources of the United States were finite and were being degraded to an unacceptable degree by man's activities, resulted in an unprecedented attempt to reverse the deterioration of these resources. These efforts have now become more searching as evidence accumulates of the possible health effects of low levels of certain inorganic and organic constituents of water. The investigation of long term effects must, in the short term, depend on existing or current data, and there are great pressures to expand these data as soon as possible so that their relationship, if any, to current biostatistical information can be assessed. The consequence for water and wastewater laboratories is mandatory analysis of many more samples, on which many more tests are made. The most efficient way to handle this greatly increased workload is by analytical instrumentation, particularly when the instrumentation is automated as much as possible.

In discussing analytical instrumentation, the term "calibration" as used herein, refers to the entire analytical procedure in which the instrumentation is used, including those steps taken to obtain the desired precision and accuracy. A characteristic feature of most physical and physico-chemical techniques for trace analysis is the necessity for finding empirically the value of an output (digital, scale reading, graphic display) corresponding to the concentration of the constituent of interest. All of these methods require the use of standards containing known amounts of the constituent, in suitable matrices, which serve as bases of comparison in the measurements. Thus calibration is an integral part of quantitative trace analysis.

The use of standard samples performs another important function in the analysis. The goal of quantitative analysis is accuracy, i.e., the ability to approach the "true" value. Errors affecting the results may be classified as either systematic or random. The former, often referred to as determinate errors, are due to causes over which the analyst has a degree of control, and their effect may be subject to reduction, elimination, or a correction factor. On the other hand random errors are not subject to control and are present even in the absence of systematic errors. Although the magnitude of random errors can be reduced by keeping all operations as identical as possible, they are never eliminated completely. The precision of results therefore depends on random errors, including those resulting from systematic errors not completely eliminated. In this situation the distinction between precision and accuracy becomes less apparent, i.e., the precision defines the accuracy that can be achieved in the absence of systematic errors. Detailed discussion of the sources of errors is given later.

While calibration procedures must be applied to the entire analytical system, calibration of individual portions (e.g., sampling, pretreatment, transducer) is helpful for diagnostic purposes. By way of illustration, gradual drift of a zero or 100% span setting can be differentiated from faulty operation, for example a clogged line by calibration of the readout device.

2. Calibration Statistics

If a normally operating analog instrument is used to make a number of measurements on a sample, the resultant readings will not be identical to one another. The closer they are together the more precise the instrument. This idea can be put on a more quantative basis. Let us assume that we make n measurements on the unknown, obtaining the reading R_i where i goes from 1 to n. The average of arithmetic mean of the reading is:

$$\overline{R} = \frac{1}{n} \Sigma R_i .$$

The variance of the readings will be given by:

$$V = \frac{\Sigma(R_i - \overline{R})^2}{n}$$

and the standard deviation of the reading is

$$s = \sqrt{V} .$$

The standard deviation of the instrument is an inverse measure of the precision of the instrument. The smaller the standard deviation the more precise the instrument. If the instrument is well behaved and its error is made up of a number of small internal inaccuracies, then a graph of a large number of readings R_i plotted against the number of times a value occurs will be a Gaussian curve. In this case, it can be shown that there is a 50% chance that any given reading lies within 0.6915 x s where s is the standard deviation. Indeed e = 0.6915s is known as the most probable error. On the other hand the probability that a reading falls outside 3s is only 0.0013. If, in testing an instrument, a reading is found to fall say at 4s or 5s, then it is probably because the operator misread the device. However, such a value of R_i should alert the user to the possibility that there is an intermittent loose connection or similar defect in the device.

If a sample whose characteristic being measured is known very exactly, the accuracy of the instrument determines how close an individual R_i is to C_i, the known characteristic. If these differences are small the instrument can be said to be accurate.

Calibration is the procedure used to ensure instrument accuracy. If the instrument is of low or poor precision, the calibration cannot improve its precision, but it can make $\bar{R}$ as close as desired to C_i. The calibration may take one of two forms. There may be an adjustment that can be made on the instrument permitting R_i or $\bar{R}$ to be brought closer to C_i as measurements are made on one or more C_i's or standard samples. Alternatively the calibration may be in the form of a curve giving the functional relationship between R_i and C_i. Methods and means for carrying out calibration procedures is the subject of this section.

If the functional relation between R_i and C_i is linear or can be linearized it greatly simplifies plotting an accurate calibration curve. Assume that $R_i = a + bC_i$ then the problem reduces to one of evaluating "a" and "b." The first step is to make n readings using n values of C_i where i = 1 to n. From this "a" and "b" can be calculated as follows:

$$a = \frac{n\Sigma R_i C_i - \Sigma C_1 \Sigma R_1}{n\Sigma R_i^2 - (\Sigma R_i)^2}$$

$$b = \frac{\Sigma R_i^2 \Sigma C_i - \Sigma R_i \Sigma R_i C_i}{n\Sigma R_i^2 - (\Sigma R_1)^2} .$$

This is known as the method of least squares and the resulting calibration curve is free from subjective judgment and makes nearly maximum use of the measurements made.

In most quantitative analytical methods the foregoing is complicated by many sources of error, both determinate and indeterminate. They include sampling errors (which may not be apparent until the analytical results are obtained), errors due to handling (chemical operations, extractions, storage) and errors due to sample presentation to the instrument. The statistical treatment is the same as for calibration errors, but it is important to recognize that these additional factors will cause variations in the results of a method which cannot properly be ascribed to the instrumentation.

For trace determinations, reliable standard samples may not be available for the desired low concentrations, but only for relatively high ones. In these cases, one is forced to extrapolate the calibration function into the desired low range, sometimes through several orders of magnitude. This task requires a high degree of critical judgment because small deviations at the start may cause grave systematic errors in the low range.

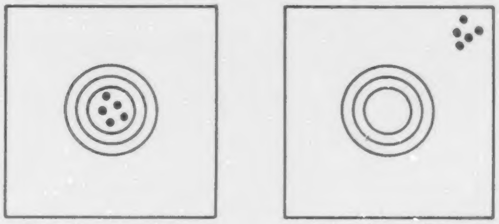
In order to make extended extrapolation practicable, two basic requirements should be fulfilled:

(a) *The calibration function must be linear.* If not, it must be 'linearized' by a suitable transformation as discussed earlier, or to suitably arrange the standardization function such that it is graphically linear. This can be accomplished by, for example, a semi-logarithmic or a logarithmic representation.

(b) The calibration function must be established for the net measure only; *the blank portion of the measure must be eliminated.*

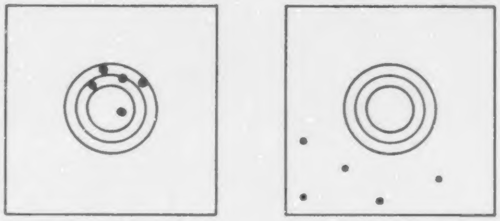
(c) A program to assure traceability to a common reference standard, referred to as a primary standard, must also be included.

Accuracy, as discussed, normally refers to the difference (error or bias) between the set of results measured and the value which is accepted as the true or correct value for the quantity measured. Precision refers to the extent to which a given set of measurements agrees with the mean of the measurements. Figure 1 illustrates examples of accuracy and precision in target shooting.



Precise and accurate

Precise and inaccurate



Accurate and imprecise

Inaccurate and imprecise

Fig. 1. Random and systematic errors.

There are two broad classes of error which should be recognized: (1) determinate or bias (systematic) errors and (2) indeterminate or random errors. Bias errors are due generally to poor procedures and may be caused by equipment and/or personnel. Systematic human errors are reduced by using standard procedures. Systematic equipment errors may be accounted by proper calibrating techniques which result in the generation of calibration curves of the type shown in Fig. 2. Bias errors are often constant for each case and of a unidirectional nature (positive or negative). Thus, if the magnitude and direction of the errors are known, their effect can be taken into account and the following expression applies

$$x_c = x_0 \pm e_0$$

where

x_0 is the observed value

e_0 is the absolute error (bias) at the condition at which the observation is made.

Instrumentation bias is not necessarily a limiting factor if it can be evaluated by calibration.

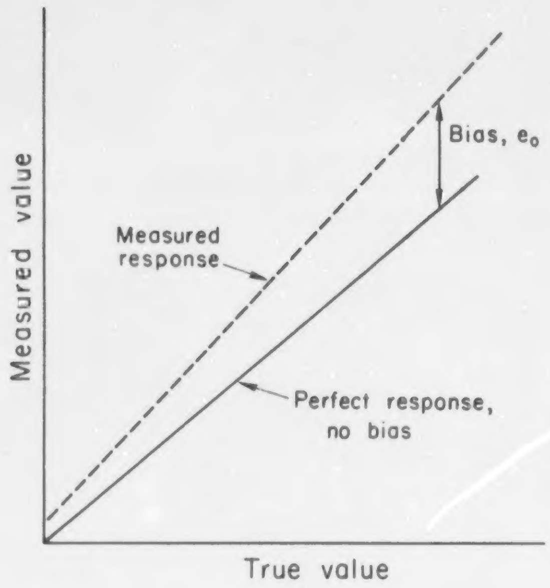


Fig. 2. Typical calibration curve.

Random errors are as likely to be positive as negative and their specific magnitude and direction cannot be predicted for each measurement. They occur because in each test there are a number of experimental variables, each of which causes a small uncontrolled error. Random errors are described by laws of probability and statistics and are usually normally distributed. Information on standardization statistics may be obtained from Standard Methods, (14th edition (Ref. 2), The Book of ASTM Standards, Part 31 (Ref. 3), Chemical Analysis (Ref. 4), and the draft Manual on Analysis for Water Pollution Control (Ref. 5).

Calibration techniques depend in a large part upon an understanding of the operation of the instrument and the manner in which the instrument is to be used. Usually, standardization involves a determination of instrument response of at least 3 points on a calibration curve. Knowledge of whether the response is linear or exponential is important, particularly if extrapolations of the standard curve are necessary. Before the response of the instrument can be calibrated, the matrix in which the constituent(s) of interest occurs must be known. The matrix may be definable at the time of sample collection, or more often by a properly sequenced quantitative analysis. When the matrix is shown to contain interferences, several techniques are available, including standard addition, and preparing standards which contain the interferences as they occur in the sample.

The accuracy of any instrument calibration depends upon many factors, but it must be remembered that indeterminate errors are not necessarily random. The most probable cumulative error can then be determined according to the following equation:

$$E_c = \sqrt{E_1^2 + E_2^2 + E_3^2 + \cdots} \quad .$$

As mentioned above, other factors in sampling and handling are often of much greater variability than the response of the instrument.

The sensitivity and range of an instrument's response are prime considerations in the calibration of an instrument.

3. Sources of Error in Water Calibration

Errors in water quality measurements are classified as either determinate or indeterminate (Fig. 1). Calibration is aimed at increasing the accuracy of the analysis by eliminating determinate errors, and minimizing indeterminate errors.

a. Bias Error

Bias errors are those errors over which the analyst exercises some degree of control, for example by maintaining clean glassware. They are said to be present when the analytical result is either higher or lower than the true value, and the mean of repeated measurements on portions of the same sample does not approach the true value as the number of measurements increases.

When bias errors occur, the results are biased; the term bias has been used synonymously with the term systematic error (Ref. 5).

Instrument drift is an example of a bias error which is avoidable by calibration of the instrument zero and 100% span settings. Modern instrumentation generally has low electronic drift rates. For example, a typical manufacturer's specification lists electronic drift rate as follows:

± 0.5% of full scale per 4 weeks; ± 1 digit or ± 0.3% per 24 hours; ± 0.001 absorbance units per hour.

The overall stability of automated instruments during unattended operation is particularly important in the generation of reliable data. The automated equipment should be evaluated for its performance during extended operation. For example, see Table (1) which lists drift data obtained from a TOC/TC automated analyzer. For this test, drift was defined as the net change in instrument output with time at a constant TOC concentration with unadjusted continuous operation. No measurable change was observed for zero drift, while the span drift ranged from zero to maximum of 0.8% full scale per day (Ref. 6).

In summary, bias errors are assumed present when results are greater or smaller than the true or calibrated value. Bias errors are minimized by good laboratory practice: e.g., checks for drift, cleanliness of sample transport lines, and use of reliable standards for calibration.

b. Random Errors

Random or indeterminate errors may be intrinsic to the instrumental analytical system; they are not controllable by the analyst. Examples of sources of errors in water analysis systems are the following: (1) nature of sample (e.g., fresh water, waste water), (2) sample chemical pretreatment (e.g., oxidation, precipitation), and (3) instrumental sensitivity. In many water analysis systems, the nature of the sample or the sample pretreatment cannot be changed. However, the type of instrumental method used for the measurement may be optional. In this case, the analyst should select a method with high sensitivity in order to increase the precision, reduce the error, and therefore decrease the number of replicate measurements required to arrive at the true value. This is because the precision of the result depends on random errors, and the precision defines the accuracy that can be achieved in the absence of systematic errors. Tables (2) and (3) list sensitivities for a number of important instrumental methods.

The magnitude of random errors is indicated by the scatter about the mean value of results of repeated measurements on portions of the same sample. Both the sign and magnitude of the error show a random scatter, and frequently cannot be predicted beforehand with exactness. The degree of scatter of the results defines the precision of the measurement which decreases as the random errors increase. Some random error is always present by the very nature of the physical world.

In summary, the *precision* of an instrument is its reproducibility; the *accuracy* is how close its reading is to the true value. A systematic error causes a loss of accuracy, and it may or may not affect the precision depending upon whether the error is constant or variable. Random errors cause a lowering of reproducibility, but by making sufficient observations it may be possible to compensate for the scatter so that the accuracy is not necessarily affected. Statistical treatment, can be properly applied only to random errors, but it is not known in advance whether the errors will be truly random. However, the laws of probability can be applied to determine whether nonrandomness (e.g., trends, discontinuities, clustering) is a factor. If such is the case, an effort should be made to locate and correct the systematic causes. (Ref. 4).

4. Interlaboratory Comparisons

Interlaboratory comparison is accomplished by the comparison of results obtained among a number of cooperating laboratories on the same water standard. Such a standard may be a synthetic solution prepared by dissolving pure (99.9+%) metal in the minimum amount of acid and diluting to volume with the highest grade reagent water. Another type of standard is prepared by adding a solution of a single metal to a sample of fresh (natural) water. These are made up to simulate actual field conditions to the greatest extent possible, with matrices being comparable. Each participating laboratory is then sent a representative sample from the bulk standard for analysis by the method under evaluation. The analyses provided by each participating laboratory are then treated statistically to calculate both the precision (reproducibility) and accuracy. The precision is usually expressed by the standard deviation, and the accuracy by the standard error.

Interlaboratory comparison of data is useful when a water analysis method is being considered, e.g., for regulatory considerations or for contribution to a data bank. By and large, collaborative testing is used to control the quality of analytical work. It is found that without interlaboratory collaborative tests errors often arise in using an analytical method that otherwise will not be detected. These errors are due to one or more of the following causes: (1) careless preparation of the sample for analysis, (2) the presence of interfering substances in one location and not in another, (3) the presence of impurities in the analytical reagents, (4) a seemingly trivial but in reality, important difference in the analytical procedure, (5) dirty equipment, and (6) use of instrumentation from different manufacturers which have different performance characteristics.

TABLE. 1. Zero and Total Drift (Ref. 6)

Test No.	Sample	Carbon Conc. (mg/ℓ)	Model	Duration (days)	Analyzer Reading (mV.)		Full Scale (mg/ℓ)	Observed Change		
					Start	End		% Full Scale	(mg/ℓ)	% Full Scale/Day
1	$KHC_8H_4O_4$	0	TOC	0.5	0.56	0.56	500	0	0	8
2	$KHC_8H_4O_4$	124	TOC	2.5	20.5	21.5	400	1.8	7	0.7
3	$KHC_8H_4O_4$	192	TOC	2.1	23.9	24.8	500	1.4	7	0.7
4	$KHC_8H_4O_4$	100	TOC	14	24.5	19.0	500	-11.0	-55	-0.8
5	$KHC_8H_4O_4$	200	TC	11	12.2	13.7	1000	2.3	23	0.2
6	$KHC_8H_4O_4$	180	TC	6	11.8	11.0	1100	-1.1	-12	-0.2
7	$KHC_8H_4O_4$	190	TC	1	13.2	13.2	1000	0	0	0
8	Primary Sewage	60	TC	1	5.0	4.6	1000	-0.4	-4	-0.4
9	Ethyl Acetate	80	TOC	2.5	23.2	23.9	230	1.7	4	0.7

TABLE 2. Sensitivity of Instrument Methods Commonly Used for Analyses in Water

Instrumental Method	Sensitivity (μg/l)	
Automated Total Organic Carbon	10,000	
Polarography	100	1000
Wet Chemical Analyzer	100	1000
Molecular Absorption	100	1000
Atomic Absorption (Flame)	100	1000
Atomic Emission	100	1000
Square Wave Polarography	10	100
Sweep Voltammetry	10	100
Emission Spectroscopy (Arc)	10	100
X-Ray Fluorescence	10	100
Automated Ammonia	10	10
Pulse Polarography	1	10
Molecular Fluorescence	1	10
Spark Source Mass Spectrometry	1	10
Anodic Stripping	0.1	10
Neutron Activation	0.1	10
Atomic Absorption (Flameless)	0.1	10
Chemiluminescence	0.1	10
Emission Spectroscopy (Plasma)	0.1	10
Cold Vapor Hg Analyzer	0.2	0.2
Automated Cold Vapor	0.2	0.2
Turbitity	0.02	NTU

TABLE 3. Analytical Methods Commonly Used for the Determination of Organic Compounds in Water

Method	Approximate Sensitivity MDL[a]	
	Instrument (gm)	Method (gm/l)
Gas Chromatography	10^{-12}-4×10^{-9}	5×10^{-9}-5×10^{-7}
Direct Aqueous GC	10^{-9}-4×10^{-9}	10^{-3}-5×10^{-6}
Gas Chromatography/ Mass Spectroscopy	10^{-9}-10^{-7}	10^{-8} 5×10^{-6}
Direct Aqueous GS-MS	10^{-9}-10^{-7}	10^{-3}-5×10^{-2}
Infrared Spectroscopy	10^{-6}-10^{-4}	10^{-5}-10^{-3}
Ultra Violet Spectroscopy	10^{-9}-10^{-7}	10^{-7}-10^{-6}
Thin-Layer Chromatography	5×10^{-8}-10^{-7}	5×10^{-7}-10^{-5}
Liquid Chromatography (UV Detector)	10^{-8}-10^{-6}	10^{-5}-10^{-3}

[a] Minimum detectable limit.

The Youden two-sample technique is commonly used for evaluating interlaboratory performance. (Ref. 5). This technique requires each participating laboratory to make one single determination on each of two samples; the number of laboratories can conveniently range up to one hundred.

In evaluating the data, both the mean value ($\bar{R}$) and the standard deviation, s , are calculated for each sample and each constituent (if more than one) using the results from all the laboratories. Next, all results exceeding $\bar{R} \pm 4s$ are rejected as indicating laboratories with systematic errors, and a new $\bar{R}$ and s calculated using the remaining data. One evaluation of the remaining data is to calculate the percent deviation from the true value.

Figure (3) shows the result on interlaboratory testing of four samples of mercury in water (Ref. 7). As seen, the between-laboratory agreements tend to deteriorate at mercury levels between 0.16 to 1.16 μg/l.

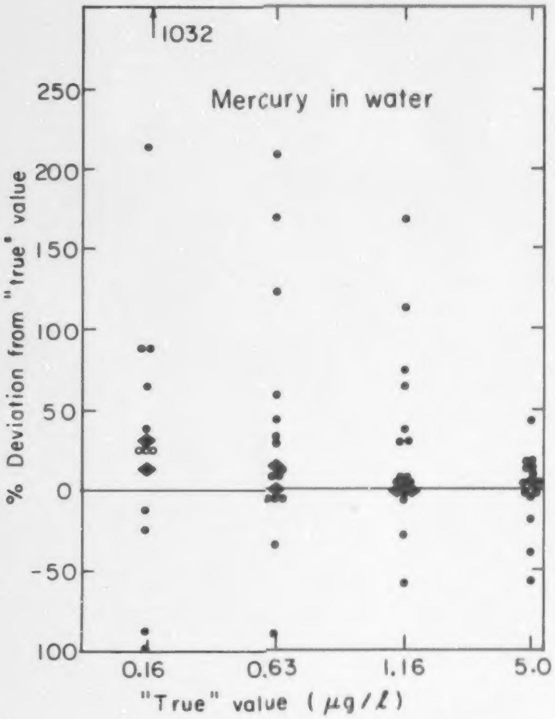


Fig. 3. Results of interlaboratory testing of four samples of mercury in water. (Ref. 7).

For interlaboratory comparison data on other pollutants and water quality standards, the reader is referred to the appropriate sections in Standard Methods, (14th Edition), and the EPA Manual.

In summary, interlaboratory collaborative tests provide valuable information on both the reliability of data, and the kind of precision and accuracy achievable.

B. SYSTEMS STANDARDIZATION

The number of steps or modules required for measuring a water quality parameter depends to a large extent on whether the analysis is made in the field or in the laboratory. For example, laboratory analysis involves measurements made on grab samples which may have an added preservative. A continuous field monitor of the sensor type, on the other hand, may be immersed directly into the water stream. Thus, calibration methods must include the entire system and not simply the instrumental measurement.

1. Laboratory Manual Instruments

Calibration methods for laboratory manual instruments can be classified as based on one of the following five types: (1) certified standards, for example, those available from the National Bureau of Standards, (2) comparison of the method being standardized with a commonly accepted method, (3) standard additions in which a small amount (e.g., µg) of the constituent is added to the water sample being analyzed, (4) synthetic standards prepared by dissolving the constituent in an aqueous solution, (5) theoretical relationships, for example coulometric analyses based on Faraday's Law. Those most commonly used for water analyses are based on certified reference standards,* calibration curves, standard additions, and synthetic standards: see Morrison (Ref. 8).

a. Certified Standard Reference Materials

Standard Reference Materials (SRM's) prepared and issued by the National Bureau of Standards are used as primary standards. The SRM's are gases, solutions or solids of carefully characterized materials containing accurately known quantities of an aqueous chemical pollutant (e.g., metal) or known magnitude of a physical parameter of water (e.g., pH).

Each SRM is designated by a distinguishing name and unique number; each sample of the SRM is of identical characterization with every other sample bearing the same designation within the limits required. When necessary, the SRM will be given a serial number and an individual calibration. In June 1975, NBS offered over 800 different SRM's; however, unfortunately only a very few are specific for water quality monitoring. Table (4) lists SRM's for water quality research and monitoring measurements. The dry, powdered orchard leaves and glass wafers are useful in calibrating the instrumental portion of the neutron activation, x-ray fluorescence, emission spectrometry and spark-source mass spectrometry techniques.

TABLE 4. National Bureau of Standards Certified SRM's for Instrumentation Calibration

SRM Number	Material	Certified Elements or Property
1641	Water solution	Hg - 1.49 mg/ℓ
1642	Water solution	Hg - 1.18 µg/ℓ
1571	Solid-orchard leaves	As - 14 µg/g
		B - 33
		Cd - 0.11
		Cu - 12
		Fe - 300
		Pb - 45
		Mn - 91
		Hg - 0.155
		Ni - 1.3
		Zn - 25
		N - 2.76%
		P - 0.21 %
614-615	Glass wafer (1-mm and 3-mm diameter)	Co - 0.71 ppm
		Cu - 1.34
		Pb - 2.32
		Ag - 0.42
682	High-purity metal	Zn
185d	Acid potassium phthalate	pH 4.004 at 25°C
186Ic, 186IIb	Potassium dihydrogen phosphate, disodium hydrogen phosphate	Mixed to give pH 6.865 at 25°C

The SRM's are of importance for both intralaboratory and interlaboratory calibration because the true value of a particular constituent is accurately known. Thus, for interlaboratory cooperative tests, the ability of the participating laboratories to get the true value (zero bias) as well as to agree with each other (e.g., precision) is determined.

b. Standard Additions

In the analysis of complex materials both matrix and interelement effects are the main contributors to systematic errors in many spectrometric methods. Therefore, the use of certified standards or the independent method of analysis approach on similar materials help to compensate for these complexities.

Another approach that is sometimes used is the method of standard additions, where a small known concentration of the desired species is increasingly added to several samples of the unknown material. The resulting samples as well as an untreated one are then analyzed. The response readings from the particular instrument are then plotted linearly against the concentrations, and the amount of unknown species present is determined by extrapolating a line to the abscissa. (Fig. 4). If the line is not linear, often a transformation can be performed such as the conversion of light absorption to absorbance. The best line which can be fitted to the data minimizes the sum of the squares of the vertical distance between data points and the constructed lines, referred to as the line of least-squares. (See Section 2).

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*For water analysis the only NBS certified standard available is for mercury.

Standard addition method is widely used in flame emission, atomic absorption, and spectrophotometric techniques.

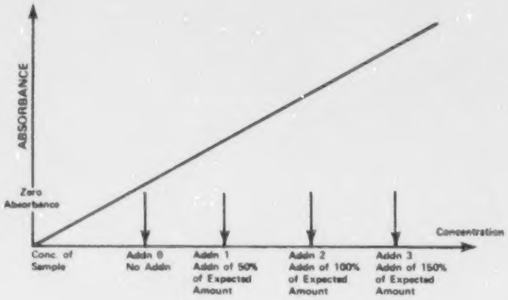

Fig. 4. Standard addition plot for atomic absorption analyses. (Ref. 5).

c. Synthetic Standards

The intent of these standards is to simulate or anticipate analyses of actual field samples. These standard synthetic samples are used for intercalibration among laboratories of instrumental methods to establish statistical precision and accuracy data. For example, Standard Methods, 14th edition, lists a synthetic standard for the dithizone method for Pb of the following composition of metal dissolved in distilled water as shown in Table (5). The sample was analyzed for Pb by 43 laboratories, with a relative standard deviation of 42.1%, and a relative error of 8.5%.

An example of a synthetic sample prepared by dissolved metals in water samples is that prepared by the Quality Assurance and Laboratory Evaluation Branch of the Methods Development and Quality Assurance Research Laboratory of the EPA in Cincinnati, Ohio. Six synthetic samples containing varying levels of Al, Cd, Cr, Fe, Mn, Pb and Zn were distributed for interlaboratory calibration of the atomic absorption method for Pb. The results were as follows (Table 6, Ref. 5).

TABLE 5

Metal	Concentration, μg/ℓ
Pb	70
Al	500
Cd	50
Cr	110
Cu	470
Fe	300
Mn	120
Ag	150
Zn	650

TABLE 6

Number of Labs	True Values μg/liter	Mean Value μg/liter	Standard Deviation μg/liter	Accuracy as % Bias
74	367	377	128	2.9
74	334	340	111	1.8
64	101	101	46	-0.2
64	84	85	40	1.1
61	37	41	25	9.6
60	25	31	22	25.7

2. Stability of Calibration

The problem of how long and under what circumstances the calibration values derived for a given analytical procedure remain valid is of importance for the critical assessment of a procedure and of the analytical results produced by it. Stability of calibration involves two aspects:

(a) the sensitivity of the analytical procedure to variations of experimental parameters, and

(b) the extent to which one has control over the parameters to keep the experimental conditions constant or to take into account the influence of changing parameters by suitable measurements and corrections.

Complex analytical procedures are usually susceptible to parameter changes, since it is difficult to reduce all of the variations simultaneously and throughout the whole range. Frequent calibration is mandatory.

3. Calibration of Automated Analyzers

Automated analyzers include both laboratory automated equipment (e.g., Technicon Auto Analyzer), and continuous field monitors (e.g., Ionics Mercury Monitor). Calibration of both classes of automated analyzers are discussed here.

Laboratory automated equipment is primarily centered around the Technicon Auto Analyzer using methods developed by the EPA. These methods are mostly based on the manual laboratory procedures given in Standard Methods, 14th edition. Calibration of the automated methods is accomplished by adding standards containing accurately known concentrations of the constituent to the sampler tray containing the samples being analyzed. For example, in the automated colorimetric phenate method for ammonia, a stock solution standard is prepared by dissolving 3.819 g anhydrous ammonium chloride in 1000 ml distilled water. From the stock solution, standard solutions are prepared to cover the concentration range of interest. These standards are loaded into the sampler tray in order of decreasing concentration of ammonia and analyzed.

Continuous field monitors are based either on sensors or an automation of manual laboratory procedures. The dissolved oxygen probe and pH electrode are examples of field monitors based on sensors. See Appendix I for recommended procedures for sensor calibration. The cyanide and phosphate field analyzers are examples of automated laboratory procedures; they are calibrated in the field using built-in standards.

C. CALIBRATION OF WATER QUALITY ANALYSIS INSTRUMENTATION

In this section specific examples of the application of systems calibration to water analysis instrumentation are given. It is not possible to cover all chemical and physical constituents; the discussion which follows centers on typical examples of important ones. For a more comprehensive coverage, the reader is referred to Standard Methods, 14th Edition; ASTM, Part 31; and The EPA Methods Manual.

1. Metals

The metal content of water samples is most commonly analyzed by laboratory instrumentation; discussion in this section will be limited to the commonly used laboratory systems. Mercury is treated separately because of the different analytical system.

a. Atomic Absorption

Standards for metals are usually prepared by dissolving pure (e.g., 99.9%) metal or metal compounds in reagent grade water which has a low background metal content (e.g., < 10 μg/ℓ) to ensure a low blank reading. Using modern methods which combine both distillation from an all-quartz apparatus and mixed-bed ion-exchange, exceptionally pure water can be obtained. Water of such high purity is a prerequisite to trace (e.g., < 100 μg/ℓ) metal analyses for it determines in part the magnitude of the blank and thus the limit of detectability (Ref. 9).

The two most commonly used atomic absorption methods for metals are standard curves and standard additions. Standardization curves are discussed first, using Cd as an example.

In Standard Methods, 14th Edition, stock Cd solutions are prepared by dissolving 100.0 mg of Cd metal in a solution composed of 20 ml distilled H_2O and 5 ml concentrated HCl. The mixture is heated to accelerate dissolution of the Cd; the resulting solution is transferred to a 1000-ml volumetric flask, and diluted to the mark with distilled water. After thorough mixing, the Cd standard solution is transferred to a polyethylene bottle. The concentration of this stock solution is 100 μg/ml (100 mg/1). From this stock solution, solutions of Cd are prepared for standardization purposes by pipetting 10.0 ml of the stock solution and 10 ml of concentrated HCl into a 1000-ml volumetric flask, and diluting to the mark with distilled water. The HCl is added to prevent the loss of Cd by hydrolysis and precipitation reactions (Ref. 2). This standard solution of Cd has a concentration of 1 mg/1; it should be prepared fresh daily.

Both the EPA and the USGS recommend preparation of stock Cd standards by different procedures than the above. A weighed quantity (e.g., 1.142 g) of reagent grade CdO is dissolved in 5 ml of HNO_3 and the solution diluted to 1000 ml with distilled water. This stock solution is further diluted to prepare the standard solutions for the calibration curve.

An example of atomic absorption calibration procedure for Pb in water is the study on the "Determination of Trace Metals in Power Plant Effluents," (Ref. 10). Measurements were made using two Perkin-Elmer Model 306 instruments equipped with both HGA-2000 and HGA-2100 graphite flameless excitation sources. Readout was accomplished using Perkin-Elmer Model 056 recorders. Standard curves were prepared from stock solutions containing 1000 mg/1 of the metal, and pipetting μl quantities into the furnace. See Figs. 5 and 6 for the Pb calibration curve. Table 7 lists the HGA-2100 operating parameters.

A good application of the standard additions method is given by Julshamn and Braekkan on determining trace metals in fish tissues (Ref. 11).

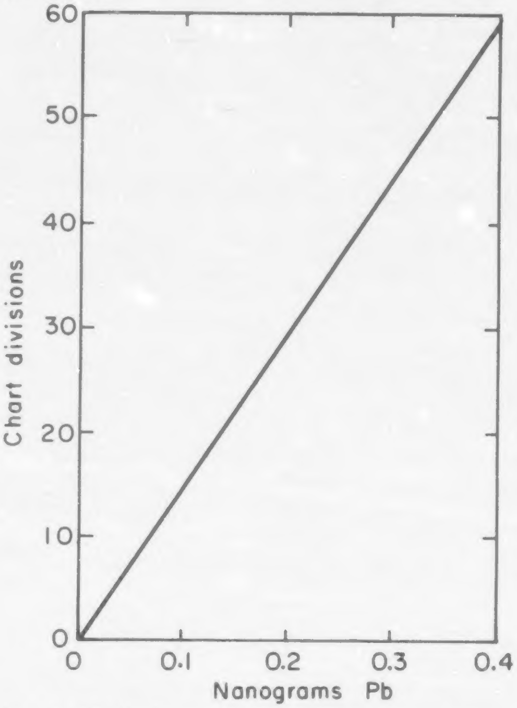

Fig. 5. Calibration curve from 0-0.4 ng Pb measured at 283.3 nm using 3X expansion.(Ref.10).

A typical calibration curve based on the method of standard additions is shown in Fig.7. All lines were plots of regression equations obtained from samples without and with the addition of 5, 10 and 15 μg Fe, corrected for

TABLE 7. HGA-2100 Operating Parameters (Ref. 10)

Element	Wavelength, nm	Spectral Band Width nm	Temperature, °C Drying	Charring	Atomizing
As	193.7 (EDL @ 6w)	0.7	100	600	2400
Cd	228.8 (EDL @ 3.5 w)	0.7	100	250	1900
Cr	357.9	0.7	100	1100	2400
Cu	324.7	0.7	100	900	2400
Fe	248.3	0.2	100	1100	2100
Mn	279.5	0.2	100	900	2400
Ni	232.0	0.2	100	950	2400
Pb	283.3	0.7	100	700	2500
Se	196.0 (EDL @ 8 w)	2.0	100	700	2400

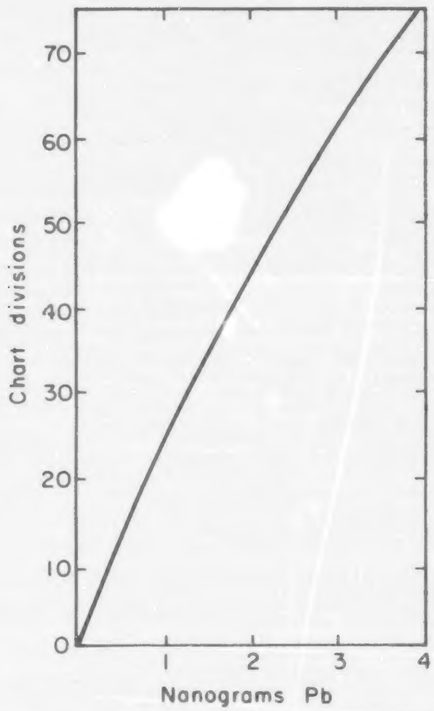

Fig. 6. Calibration curve from 0-4.0 ng Pb measured at 283.3 nm using 3X expansion. (Ref. 10).

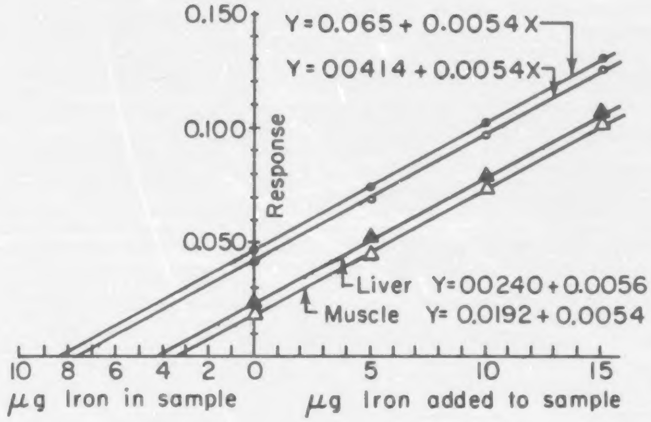

Fig. 7. Calibration curves for the determination of iron by the standard addition method. (Ref. 11).

the blank reading. The Fe content was read at the point where the lines intersect the zero response axis. The lines were calculated to fit the linear regression equation

$$y = a_0 + a_1X$$

y = response; X = μg Fe; a_0 = intercept; a_1 = slope.

All curves for Fe, Zn, Cu, Mn, Pb and Cd were highly linear with most having a correlation coefficient > 0.997. This indicated that the precision of the method was good, and that measurements were taken in the linear range of the regression curves for the different elements. See Table 8 for analytical results based on statistical treatment of the data.

TABLE 8. Regression Analysis of Curves Based on Standard Addition for Determination of Fe, Zn, Cu, Mn, Pd and Cd. (Ref. 11).

	R	α_0	α_1	1	σ(1)
Iron(Fe)					
Muscle	0.998	0.0192	0.00543	3.54	0.182
Roe	0.999	0.0414	0.00548	7.55	0.421
Soft roe	0.998	0.0365	0.00540	8.61	0.473
Liver	0.998	0.0240	0.00560	4.28	0.227
Zinc(Zn)					
Muscle	0.998	0.0241	0.00432	5.57	0.210
Roe	0.999	0.1641	0.00432	38.0	0.981
Soft roe	0.999	0.0513	0.00436	11.8	0.261
Liver	0.997	0.0251	0.00433	5.80	0.228
Copper(Cu)					
Muscle	0.999	0.0063	0.00810	0.78	0.083
Roe	0.999	0.0098	0.00805	1.06	0.100
Soft roe	0.999	0.0086	0.00815	1.22	0.110
Liver	0.997	0.0165	0.00830	1.99	0.181
Manganese(Mn)					
Muscle	0.997	0.0032	0.01170	0.27	0.081
Roe	0.999	0.0085	0.01175	0.72	0.120
Soft roe	0.999	0.0060	0.01155	0.52	0.103
Liver	0.999	0.0044	0.01195	0.37	0.083
Lead(Pb)					
Muscle	0.999	0.0018	0.01560	0.12	0.072
Roe	0.999	0.0155	0.01610	0.10	0.080
Soft roe	0.999	0.0006	0.01620	0.04	0.085
Liver	0.999	0.0024	0.01590	0.15	0.070
Cadmium(Cd)					
Muscle	0.997	0.0033	0.1463	0.023	0.0152
Roe	0.999	0.0010	0.1444	0.007	0.0130
Soft roe	0.999	0.0015	0.1450	0.010	0.0080
Liver	0.999	0.0047	0.1474	0.030	0.0141

α_R = correlation coefficient
a_0 = y = intercept, regression equation is defined as $y = a_1 X + a_0$, where X is concentration in μg/0.25 g dry matter
a_1 = slope
1 = $- a_0/a_1$ calculated for X (Y = 0) = 1
σ(1) = standard deviation = $\sigma(- a_0/a_1)$

b. UV-VIS Spectrophotometer (Colorimeter)

Calibration curves are the most commonly used method to calibrate colorimeters for metals-in-water analyses. Standard solutions are typically prepared by dissolving the pure metal in dilute acid, and generating the calibration curve (usually linear) by running the standards through the analysis procedure. The concentration of metal in the water sample usually is read from the standardization curve after correction for the blank reading.

For specific metals, the reader is referred to the appropriate sections in Standard Methods, 14th Edition, and the ASTM Annual, Part 31.

c. Neutron Activation

Calibration for neutron activation analysis is commonly carried out by exposing -- with the sample to be irradiated -- a standard containing a known weight of the metal being determined. The weight of the element being measured is then calculated from the relationship:

$$W_x = \frac{W_sA_x}{A_s}$$

W_x = Weight of element being measured
W_s = Weight of Standard
A_x = Activity of element being measured
A_s = Activity of standard.

For multielement analyses, standard solutions containing 5 to 10 elements at optimum concentration are prepared. In this way, only a few standard capsules need to be included in large set of samples being analyzed. The standards should be in as similar a matrix as possible to that of the samples; for example, saline samples such as sea water should have standards dissolved in an equivalent concentration of NaCl.

For a very good review of calibration for neutron activation, the reader is referred to the report on "Neutron Activation Techniques for the Measure of Trace Metals in Environmental Samples," by Robertson and Carpenter in the H2O--Metals section.

d. X-Ray Fluorescence

Analysis with x-ray fluorescence instrumentation is carried out on thin, solid samples (ng/cm^2 to mg/cm^2), with the higher sensitivities attained on the thinner samples. The thin specimens are important in minimizing matrix effects, for example self-absorption of the fluorescent x-rays by the sample. Good discussions of the theory of x-ray fluorescence and preparation of standards are found in the H2O--Metals section of this volume, and in the paper "Trace Element Determination with Semiconductor X-ray Spectrometers" (Ref. 12).

A recent example of calibration of x-ray fluorescence spectrometers is the application of this technique to the determination of phosphorous in natural waters. Standards were prepared by dissolving reagent grade KH_2PO_4 obtained from Fisher Scientific Co. and Mallinckrodt Chemical Works in distilled deionized water. All glassware was soaked for at least 1 hour in 6M HCl, and was never exposed to phosphate-containing detergents.

A 50.0 ml portion of sample was pipetted into a 60 ml separatory funnel; this was then followed by adding 4.50 ml conc HCl and 4 ml of 0.313 M $Na_2MoO_4 \cdot 2H_2O$ to form phosphomolybdic acid. The mixture was shaken, 10 ml ethyl acetate added, and then shaken for 30 sec. After 10 min., the lower aqueous layer was removed, 10 ml of 1 M HCl added, the mixture shaken briefly, and the HCl layer removed. The ethyl acetate was then added to a 50 ml beaker, the funnel rinsed with 5 ml ethyl acetate which was added to the 50 ml beaker. Ten ml of H_2O were added to the beaker, and the contents were thoroughly stirred to mix the two layers. To the beaker, 100 ± 1 mg of silica gel was added to absorb the phosphomolybdic acid, the pH adjusted to 2.8, and the mixture stirred for five minutes. The silica gel was collected onto E. H. Sargent and Co. No. 500 filter paper (3 cm.), dried in an oven at 100 C for 10 min., and scraped into a 5 ml microbeaker containing 100 mg of cellulose powder (Whatman CF 11). Two drops of water were added, and a paste formed by stirring the mixture. The paste was pelletized under 10,000 pounds of pressure; and Mo determined by x-ray fluorescence. The Mo content is directly proportional to the phosphorous content. A typical calibration plot is shown in Fig. 8 (Ref. 13).

The plot is linear to 3000 ppb (μg/1) phosphorous. For P concentrations at the 15 ppb level, the standard deviation was 3%. For the linear portion of the curve, the correlation coefficient was 0.998 and the Student's t value was 39.4.

2. pH Value

The pH value of a water sample is usually measured electrometrically. It depends on a number of factors including the following: (1) the form of the hydrogen-ion bearing constituent (e.g., weak or strong acid), (2) the temperature of the water, (3) the presence of dissolved ions, (4) the presence of impurities such as oils, greases, or sludges, (5) the cleanliness of the glass and reference electrode system, and (6) the constancy of both electrodes.

a. Laboratory Instrumentation

The glass and reference electrode system is standardized using standard buffer solutions

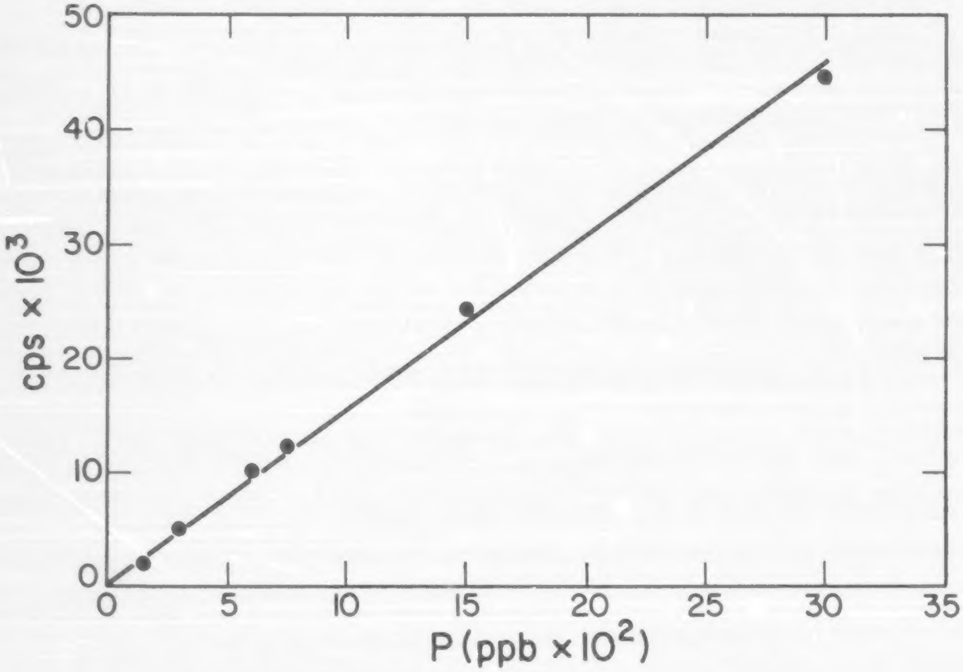

Fig. 6. Calibration curve from 0-4.0 ng Pb measured at 283.3 nm using 1X expansion. (Ref. 10).

of known pH value. The standards are prepared as needed because aged solutions may deteriorate since standard buffers have some shelf-life. Standard Methods, 14th Edition, contains a detailed discussion on preparation of buffer solutions from the buffer salts. It is recommended that certified buffer salts available from the National Bureau of Standards be used where the greatest accuracy is needed. The number of buffers should depend on the range to be covered (most water samples fall in range of 6.5-9.0).

Standard solutions are prepared by totally dissolving the correct weight of buffer power in freshly boiled distilled water with a conductance < 2μ mho at 25°C, and pH 6.7 to 7.3. The pH meter is standardized using a buffer solution with a pH value close to that of the samples.

In measuring the pH of industrial wastes, effluents and sludges, the electrodes are thoroughly rinsed with buffer solution between samples and after calibrating.

b. Continuous Field Monitors

Standardization of continuous pH monitors is discussed in Recommended Methods for Water-Data Acquisition (Ref. 14). It is recommended that the measuring system be calibrated manually at three points: pH 4, 7, and 10 using the buffer preparations described in Standard Methods, 14 Edition. See Appendix I. The calibrated accuracy of the pH measuring system is recommended to be within 1% of full scale or 0 pH unit, whichever is less, over the temperature range 0 to 40°C.

c. Manual Field Analyzers

Manual field analyzers are rugged, portable instruments that are used for pH measurements on site. The U. S. Geological Survey Methods Manual recommends that 2 or 3 standard buffers be used for calibration. (Ref. 15.) For saline water samples, a sodium correction may be required.

3. Pesticides

Analysis for trace (as low as one mg/1) quantities of pesticides in water is accomplished by laboratory instrumentation. The gas chromatographic and gas chromatographic/mass spectrometric methods are commonly used. The following is from the gas chromatographic calibration procedure given in Standard Methods, 14th Edition (Refs. 2,16):

Chlorinated pesticide stock solution standards are prepared by dissolving 100 mg of the pure material in 100 ml of ethyl acetate. From this stock, 1.0 ml is diluted to 100 ml with ethyl acetate to give an intermediate solution. A series of increasing μl amounts (1 to 5 μl) of the intermediate solution are injected into the chromatographic column, and the peak height or peak area are plotted versus pesticide concentration to give a calibration curve. Generally, peak areas give more exact results than do measurement of peak heights. For very narrow peaks, peak height measurement is recommended (Ref. 16).

The precision and accuracy for 6 chlorinated pesticides were determined by interlaboratory calibration testing. See Table 9 (Ref. 2).

TABLE 9. Precision and Accuracy Data for Chlorinated Hydrocarbon Pesticides Method (Ref. 2)

Pesticide	Conc. μg/l	No.of Labs	Relative Standard Deviation %	Relative Error %
p,p'DDT	0.50	36	38.2	5.6
	5.0	31	24.0	2.2
	29	32	24.7	2.6
Dieldrin	0.25	32	35.7	14.0
	5.0	37	42.2	7.2
	15	29	20.2	10.9
Endrin	0.10	31	38.8	16.0
	1.0	34	35.4	24.7
	10	31	16.9	8.5
Heptachlor	1.0	36	67.3	16.3
	7.5	36	41.8	19.5
	15	34	32.3	14.7
Heptachlor epoxide	1.0	33	20.6	7.0
	7.5	35	22.7	1.1
	15	36	25.4	2.5
Lindane	0.50	36	36.6	10.2
	5.0	38	42.6	13.2
	25	29	23.7	12.5

Further information on calibration of pesticides may be obtained from Standard Methods, 14th Edition, and Guidelines on Analytical Methodology for Pesticide Residue Monitoring (Ref. 16).

4. Biochemical Oxygen Demand (BOD)

Biochemical oxygen demand is included here as an example of a water quality parameter wherein the precision but not the accuracy can be determined. It is an empirical test; accuracy cannot be determined because standards which can be added in known quantities for calibration are not available.

Precision data were obtained for BOD by an interlaboratory calibration test using a glucose glutamic acid mixture. Each of 34 participating laboratories used its own seed material (settled stale sewage). The geometric mean of all results was 184 mg/1 and the standard deviation of that mean was ± 31 mg/1 (17%). (Ref. 2).

D. SUMMARY AND RECOMMENDATIONS

In summary, calibration of water quality instrumentation is largely a manual operation which involves the use of standards which contain accurately known concentrations of the pollutant. The standards are contained mainly in a solid or liquid matrix. Statistical methods are increasingly important in evaluating both intralaboratory and interlaboratory calibration procedures. Only a few standards designed for water quality instrumentation are currently available.

After reviewing the current status of water instrumentation standards and calibration procedures, some general observations are appropriate. While current standards are adequate in some respects, there are still a number of inadequacies. The optimum future standards and calibration activities should include the following:

1. Preparation and availability of certified water standards which contain pollutants at ambient level concentrations. These are needed in establishing background levels of pollutants which fall in the range $< 50\ \mu g/\ell$. The Hg $1.18\ \mu g/\ell$ solution standard will be most helpful for calibration at baseline levels.

2. Calibration methods for calibrating automated continuous field monitors. These instruments are being increasingly used both for point-source and ambient monitoring; reliable calibration procedures are needed to insure the validity of the data. The Task Group on Automatic Water-Quality Monitors has issued recommended methods for calibration of sensor-type automated monitors.

3. Use of statistical techniques for examining the accuracy and precision of trace methods, and for calculating the best calibration curve (line) for instrumental methods. Currently, calibration at trace levels have poorer precision (reproducibility) than at high concentrations. The data points are more scattered, and operator judgment in drawing a straight calibration line may vary widely.

E. ACKNOWLEDGMENTS

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G. TABLES OF MANUFACTURERS OF CALIBRATION STANDARDS

TABLE 1

Standards for Physical Parameters

Physical Parameter	Source of Standard	Manufacturer's Description	Range	Cost
	Delta Scientific	Mini-Tester, Model 22-91	0-500 ppm	$145
	Hach Chemical Company	Platinum-cobalt solution, 1414-11, 4-6 months stability	500 units	$8.75/pint
	LaMotte Chemical Products Company	1. Nessler tube, NT-C, Code 4345	Trace Amounts	$84
		2. Octet comparator, CWA, Code 7611	APHA Values	$24.95
		3. Special comparison tubes, CT-PC, Code 7523	*	$ 9.95
		4. Octet comparator, FLU, Code 5907	For lakes, rivers, bays	$19.95
Odor, Taste		Distilled Water	*	*
pH	Aquatronics, Inc.	Solution	4.0; 9.0	$3.50/pint
	Beckman Instruments, Inc. Process Instruments Div.	1. Powdered buffer	4.01-12.45	$9.00-13.00
		2. Solution	4.01; 7.00; 10.0	$5.50/quart
	Brinkmann Instruments, Incorporated	Solution	4.64; 7.15	$4.30/250 ml
	Chemtrix, Inc.	Buffer capsules	2.00-12.00	$2.75/12 capsules
	Corning	Buffer salt	4.01; 7.00; 10.00	$6.50/gram
	Delta Scientific	Color disc outfits	Each disc has 9 glass color standards, in steps of 0.2 pH or 0.5 pH	$35.00
	F & J Scientific	1. Hydrion universal indicator solution	1.0-11.0	$4.00/4 ml
		2. Hydrion paper	0.0-14.0	$1.25/dispenser
		3. Chemvelopes powder	2.00; 4.00; 7.00; 9.00	$3.50/6 envelopes
	Fil-Chem & Inc., Paul Frank Division	Tridicator pH paper	1-11; 0.25 pH accuracy	

(Continued)

TABLE 1. (Continued)

Physical Parameter	Source of Standard	Manufacturer's Description	Range	Cost
pH	Gallard-Schlesinger Chemical Manufacturing Corporation	Indicator papers	1-11, in units of 1 pH	$3.95/3 refills
	Hach Chemical Company	Buffer powder pillows	3.0-11.0	$2.20-3.20
	LaMotte Chemical Products Company	Octet comparators	0.2-13.6; in 0.2 pH increments	$9.95; $19.95
	Leeds and Northrup	Solutions	4.008; 6.865; 7.413; 9.18	
	The London Company	Buffer package	1.68-9.18	
	National Bureau of Standards	SRM 185c	pH 4.004	
		SRM I 861e	pH 6.863	
		SRM II 1861c	pH 7.415	
		SRM 187b	pH 9.183	
		SRM 188	pH 3.557	
		SRM 189	pH 1.679	
		SRM 191	pH 10.01	
		SRM 922	pH 7.699	
Specific Conductance	Beckman Instruments, Inc. Cedar Grove Operation	"Standard" cells; CEL-A-Y100, CEL-A-Y87	0:0100to 1.00 cm^{-1}	
	Hach Chemical Company	Sodium chloride solution, 1000 mg/l., stability > 12 months	*	$1.20/4 oz.
Temperature	Fenwal Electronics	Standardized resistance-temperature curves	40° F-100 °F	*
	National Bureau of Standards	Thermometers	Various	*
Turbidity	Amoco Service Co.	Amoco SNT (Styrene divinylbenzene	5.0 to 75.00 FTU	$100-$500 per 802
	Hach Chemical Company	1. Standard reflectance rod	5.0 JTU	*
		2. Hexamethylene-tetramine		$12.00/500 gram
		Hydrazine sulfate		$ 2.45/20 grams
	Hellige, Incorporated	Silica suspension	0-100 ppm	$57/quart

TABLE 2.

Standards for Chemical Parameters

Chemical Parameter	Source of Standard	Manufacturer's Description	Range	Cost
	Alfa Inorganics, Inc.	Ultrapure metal	*	*
Metals	Alpha Analytical Lab.	Solutions	1000 mg/l; 5000 mg/l	$18-68 per 1000 ml
	Apache Chemical, Inc.	Ultrapure metal	*	*
	ArRo Laboratories, Inc.	Solutions		
	Atomergic Chemetals Co.	Ultrapure metal	*	*
	J.T. Baker Chemical Co.	Solutions	1000 mg/l	$20/500 ml
	Brinkmann Instruments, Incorporated	Ultrapure metal	*	*
	Columbia Scientific Industries	Thin specimen x-ray calibration standards	*	*
	Conostan Dividion, Continental Oil Co.	Metallo-organic standards	10-5000 mg/ℓ	$20-$560
	Cominco American, Inc.	Ultrapure metal	*	*
	F & J Scientific	Solutions	1000 mg/l	$15-60 per 500 ml
	Hach Chemical Company	Solutions for Hg and Pb only	100 mg/l Pb; 100 mg/l Hg	$5.00/pint $3.50/pint
Cu,Mo	Hazen Research, Inc.	HRI Analytical standards	Cu: 0.078 to 0.94% Mo: 0.051 to 0.30%	$100 per 400 gram
	Materials Research Corp.	Ultrapure metal	*	*
	MCB Manufacturing Chemists	Solutions	1000 mg/l	*
	National Bureau of Standards	1. SRM 1571 orchard leaves		*
		2. SRM 606-619; trace elements (Cd, Pb only)		*
	Perkin-Elmer, Coleman Instruments Div.	Hg solution	*	$5.50/450 ml
	Spex Industries, Inc.	Ultrapure metal	*	*

TABLE 2. (Continued)

Chemical Parameter	Source of Standard	Manufacturer's Description	Range	Cost
Pesticides	Analabs, Inc.	Pesticide Standards	Solid; 0.1 to 1000 mg/ℓ	Various
	Chem. Service, Inc.	Purified Pesticides	Solid	Various
	PolyScience Corporation	1. Solution, 1.0% (w/w) in benzene	*	$65-70/5 ml
		2. Purified pesticide	*	*
Phenols	Hach Chemical Company	Phenol, ACS	*	$7.75/lb
	PolyScience Corporation	Mixture 175; Phenols (benzene, phenol, m-cresol, o-ethylphenol, p-ethylphenol)	*	* $60/5 ml; some 10 ml
Nutrients	Hach Chemical Company	Solutions:		
		1. NH_3 - N	1 mg/l	*
		2. NO_3 - N	0.3 mg/l	*
		3. PO_4 - P	1 mg/l	*
Polychlorinated Biphenyls	Analabs, Inc.	99% pure PCB Isomers	*	Various

H. APPENDIX

Recommended Methods for the Acquisition of Data Using Automatic Water-Quality Monitors (Ref. 14)

INTRODUCTION

The purpose of this document is to set forth criteria for the operation of water-quality monitors so that the data generated by the monitors will meet acceptable levels of accuracy.

The system performance requirements outlined under this chapter are not to be considered as engineering specifications. It should be recognized that in order to meet specific needs of operation, enforcement, or management, data must sometimes be collected under more rigorous criteria of accuracy and transient response than those prescribed in this document.

General

Automatic water-quality monitors of the electro-chemical and electro-physical types provide the most economical means of obtaining continuous or time-series reporting of certain water quality characteristics. Monitors of this type consist of three basic sections: the sensing elements, the signal-conditioning elements, and the data logging or display section. The sensing elements may be immersed directly in the stream, but the more common approach is to pump the sample to a sensor chamber in which the elements are located. The signal-conditioning elements convert the signals from the sensors to an appropriate voltage level proportional to the measured variable. The data logging or display section presents the measured value, usually in engineering units.

Parameters

A variety of electro-chemical and electro-physical sensors are available. The reliability of some of these for use with water-quality monitors has been demonstrated. Others developed for laboratory use may be adaptable to automatic monitoring but as yet are unproven for this application. Active research is being conducted for developing sensors to measure other parameters.

Existing sensors - unproven

Water temperature
Specific conductance
Dissolved oxygen
pH
Chloride ion
Turbidity
Oxidation-reduction potential, or redox potential
Solar radiation

Existing sensors - unproven

Bromide ion
Cadmium ion
Calcium ion
Cupric ion
Cyanide ion
Fluoride ion
Fluoroborate ion
Iodide ion
Lead ion
Nitrate ion
Perchlorate ion
Silver ion
Potassium ion
Sodium ion
Sulfide ion
Thiocyanate ion
Water hardness

Other sensors (under development)

Ammonia
Phenol
Phosphate
Nitrite
Sulphate

SCOPE

This recommendation deals with system performance requirements, sampling techniques and calibration methods for automatic water quality monitors which employ electro-chemical and electro-physical sensors to measure one or more water-quality parameters.

UNITS OF MEASUREMENT

The units of measurement used in this recommendation are degrees Celsius or Fahrenheit, micromhos, milligrams per liter, pH units, JTU (Jackson Turbidity Units) millivolts, and gram calories per square centimeter per minute.

DEFINITIONS

The following definitions will be used throughout this document.

Calibrated Accuracy

The calibrated accuracy is the difference between the indicated parameter value and its actual value. It is determined by calibrating the measuring system with an uncontaminated sensor as outlined under the section in this document entitled, "System Calibration."

Transient Response

The transient response is the rate at which the system responds to a step change. It is a function of the time constant of a first order differential response which takes the exponential form of $1 - e^{-t/T}$ where t = time and T = time constant. Although not all measuring systems follow a first order differential response, the time constant indicated for each parametric measuring system is intended for the purposes of this document to establish a minimum rate of response which all measuring systems must equal or exceed throughout the full transient period of 0 to 5T.

Stability

Stability is a measure of the length of time a measuring system, once calibrated, continues to measure the actual parameter value within the calibrated accuracy without the need for adjustment or recalibration. Stability performance is based upon the measurement of standard calibrating solutions with an uncontaminated sensor.

Temperature Compensation

Temperature compensation is an adjustment which corrects for the effect of temperature on the measuring system. In addition it may also adjust the measured value of a parameter to a selected temperature based on a known parameter-temperature relationship. Temperature compensation may be incorporated into the measuring system so that the value reported is the adjusted value. If this approach is not used, then manual or algebraic methods are necessary to obtain the adjusted value.

Contamination

Contamination is any fouling of a sensor which causes its calibrated output to shift by a discernible amount.

Representative Sample

A representative sample is a water sample whose measured values are characteristic of the body of water from which the sample has been taken.

Degradation

Degradation is any physical, chemical, or biological process which causes the characteristics of the water sample at the sensor to vary from those at the intake. For the purpose of this document any variations greater than those listed in the table below are considered excessive.

Parameter	Difference between Measured Value at the Sensor and at the System Intake
Water Temperature	±0.1°C
Specific Conductance	±0.5% of full scale
Dissolved Oxygen	±0.15 mg/l
pH	±0.05 pH unit
Chloride Ion	±1.0% of full scale
Turbidity	±1.0% of full scale
Oxidation-Reduction Potential	±6 millivolts

SYSTEM PERFORMANCE

The criteria set forth in this section pertain to the system from the sensor to the data logger, and apply to the system over environmental operation conditions ranging from -10° to 50°C with humidity levels up to 99%. Any exceptions to the above are noted in the appropriate section. For details on calibration methods for each of the following parameters, see the appropriate section under System Calibration.

Water Temperature

Calibrated Accuracy

The calibrated accuracy of the temperature measuring system shall be within 1% of full scale of ±0.5°C whichever is less.

Transient Response

The time constant of the temperature measuring system shall not be greater than one minute.

Stability

The temperature measuring system shall retain its calibrated accuracy for a period of not less than 4 weeks.

Specific Conductance

Calibrated Accuracy

The calibrated accuracy of the specific conductance measuring system shall be within 3% of full scale over the temperature range of 0 to 40°C.

Transient Response

The time constant of the specific conductance measuring system shall not be greater than 2 minutes.

Stability

The specific conductance measuring system shall retain its calibrated accuracy for a period of not less than 4 weeks.

Temperature Compensation

The data from the specific conductance measuring system shall be temperature compensated according to the characteristics of potassium chloride solution and normalized to 25°C.

Dissolved Oxygen

Calibrated Accuracy

The calibrated accuracy of the dissolved oxygen measuring system shall be within ±1% of full scale or ±0.1 mg/l, whichever is greater.

Transient Response

The time constant of the dissolved oxygen measuring system shall not be greater than 2 minutes.

Stability

The dissolved oxygen measuring system shall retain its calibrated accuracy for a period of not less than 4 weeks.

Temperature Compensation

The dissolved oxygen measuring system shall be temperature compensated so as to meet the accuracy requirements as outlined in the section under Calibrated Accuracy, above.

pH

Calibrated Accuracy

The calibrated accuracy of the pH measuring system shall be within 1% of full scale or 0.1 pH unit, whichever is less, over the temperature range of 0 to 40°C.

Transient Response

The time constant of the pH measuring system shall not be greater than 2 minutes.

Stability

The pH measuring system shall retain its calibrated accuracy for a period of not less than 4 weeks.

Temperature Compensation

The pH measuring system shall be temperature compensated so as to meet the accuracy requirements as outlined under Calibrated Accuracy, above.

Chloride Ion

Calibrated Accuracy

The calibrated accuracy of the chloride ion measuring system shall be within ±5% of full scale.

Transient Response

The time constant of the chloride ion measuring system shall not be greater than 2 minutes.

Stability

The chloride ion measuring system shall retain its calibrated accuracy for a period of not less than 4 weeks.

Temperature Compensation

The chloride ion measuring system shall be temperature compensated so as to meet the accuracy requirements as outlined in the section under Calibrated Accuracy, above.

Turbidity

Calibrated Accuracy

The calibrated accuracy of the turbidity measuring system shall be within ±5% of full scale over the temperature range of 0 to 40°C.

Transient Response

The time constant of the turbidity measuring system shall not be greater than 1 minute.

Stability

The turbidity measuring system shall retain its calibrated accuracy for a period of not less than 4 weeks.

Oxidation-reduction Potential (ORP), or Redox Potential

Calibrated Accuracy

The calibrated accuracy of the ORP measuring system shall be within ±12 millivolts when the standard buffer solutions are measured as noted in the section under System Calibration.

Transient Response

The time constant of the ORP measuring system shall not be greater than 2 minutes.

Stability

The ORP measuring system shall retain its calibrated accuracy for a period of not less than 4 weeks.

SYSTEM CALIBRATION

Calibration data for all measuring systems shall be provided in the manner described in the following paragraphs.

Water Temperature

Method

The water temperature measuring system shall be calibrated by immersing the sensor in a beaker of water and comparing the output of the measuring system to that obtained by a good grade, mercury-filled thermometer, either centigrade or Fahrenheit, which has been checked against a precision thermometer certified by the National Bureau of Standards.

Calibration Points

The temperature measuring system shall be calibrated at three points. One point is obtained by placing the sensor in a container of stirred water near zero degrees C (obtained by adding ice to a container of water). A second calibration point shall be obtained by placing the sensor in a container of stirred water sufficiently warm to produce a reading near the full scale value of the measuring system. The third point should be obtained by placing the sensor in a container of stirred water that will produce a reading near mid-scale.

Specific Conductance

Method

The specific conductance measuring system shall be calibrated by immersing the sensor in a beaker of potassium chloride standard solution and comparing the output of the measuring system to the known value of the standard solution. The potassium chloride solution should be prepared in accordance with the instructions given in Standard Methods for the Examination of Water and Waste-water, Thirteenth Edition, 1971.

Calibration Points

Each applicable range of the specific conductance measuring system shall be calibrated at three points by employing potassium chloride standard solutions at or near 15%, 50% and 100% of full scale. Each range shall be checked for temperature compensation using solutions of potassium chloride having values of specific conductance near the midscale of each range.

Dissolved Oxygen

Method

The dissolved oxygen measuring system shall be calibrated by immersing the sensor in a beaker of air-saturated water and comparing the output of the measuring system to that obtained by an analysis of the water. The water shall be stirred or made to flow with sufficient velocity such that any increase in flow or stirring shall not cause a change in the sensor output. The analysis shall be made in accordance with the Alsterberg modification of the Winkler method of dissolved oxygen determination. (Reference: Standard Methods for the Examination of Water and Wastewater, Thirteenth Edition, 1971; Methods for Chemical Analysis of Water and Wastes, 1971, Environmental Protection Agency; and Techniques of Water-Resources Investigations of the United States Geological Survey, Book 5, Chapter A1: "Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases." The water must be free of interfering substances; therefore, the use of distilled water is recommended.

Care must be taken to allow adequate time in each test for the sensor to reach equilibrium.

Calibration Points

The measuring system shall be calibrated at three points: One preferably at the zero level, one at approximately one-third of full scale, and one at approximately two-thirds of full scale. The zero level is obtained by adding a few crystals of cobalt chloride ($CoCl_2$) to a beaker of saturated sodium sulfite (NA_2SO_3) solution. Various concentrations of oxygen in air saturated water can be obtained by changing the water temperature. See "Standard Methods," pp. 480-1 for table showing saturated values at various temperatures.

pH

Method

The pH measuring system shall be calibrated by immersing the sensor in a beaker of standard pH buffer solution and comparing the output of the measuring system to the known value of the buffer solution. The buffer solution shall be prepared in accordance with the instructions given in Standard Methods for the Examination of Water and Wastewater, Thirteenth Edition, 1971.

Calibration Points

The pH measuring system shall be calibrated at three points, using buffer solutions having nominal values of 4, 7, and 10 pH units.

Chloride Ion

Method

The chloride ion measuring system shall be calibrated by immersing the sensor in a standard sodium chloride solution and comparing the output of the measuring system to the known value of the standard solution. The standard solution shall be prepared in accordance with the instructions given in Techniques of Water-Resources Investigations of the United States Geological Survey, Book 5, Chapter A1: "Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases."

Calibration Points

The chloride ion measuring system shall be calibrated at three points by employing standard solutions at or near 10%, 50%, and 100% of full scale of the range being used.

Alternate Method (Titrimetric)

The chloride ion measuring system shall be calibrated by titration of a water sample obtained from the monitoring system and using methods given in Standard Methods for the Examination of Water and Wastewater, Thirteenth Edition, 1971.

Turbidity

Method

The turbidity measuring system shall be calibrated by immersing the sensor in a beaker of Formazin solution and comparing the output of the measuring system to the known value of the standard Formazin solution. The stock Formazin solution shall be prepared in the following manner:

(1) Dissolve 10.00 grams of reagent grade hydrazine sulfate ($N_2 H_4, H_2SO_4$) in 900 ml of distilled water
(2) Dissolve 100.00 grams of pur hexamethylene tetramine $(CH_2)_6N_4$ in 900 ml of distilled water
(3) Pour the two solutions into a 2000 ml volumetric flask and dilute to 2000 ml with distilled water
(4) Allow the solution to stand for 48 hours at 20° to 22°C (68° to 72°F) during which time the suspension will develop.

The following table gives the relationship between each of the listed dilutions of the stock solution and its corresponding turbidity (in Jackson Turbidity Units).

JTU	ml of stock suspension diluted to 1.000 liter with turbidity-free water
3000	750
2500	625
2000	500
1500	375
1000	250
500	125
400	100
300	75
200	50
150	37.5
100	25

NOTE: The Formazin stock suspension is stable for approximately two weeks whereupon it should be discarded. The diluted samples are stable for no more than one week.

Calibration Points

The turbidity measuring system shall be calibrated at three points by employing standard solutions at or near 20%, 50% and 100% of full scale of the range being used.

NOTE: The zero point may be checked by immersing the sensor in distilled water.

Alternate Method

The turbidity measuring system shall be calibrated by obtaining a water sample from the monitoring system, measuring its turbidity value with a commercial turbidimeter, and then comparing this value with the output of the monitor measuring system. The accuracy of the commercial turbidimeter shall be as specified under the section on System Performance and shall be calibrated in accordance with the method under System Calibration. When possible the method described under that section should be used in preference to the alternate method also described under that section.

Oxidation-reduction Potential (ORP), or Redox Potential

Method

The oxidation-reduction potential (ORP) measuring system shall be calibrated by immersing the sensor in a beaker of standard pH buffer solution to which quinhydrone crystals have been added and comparing the output of the measuring system to the known value of the buffer solution. The buffer solution shall be prepared in accordance with the instructions given in Standard Methods for the Examination of Water and Wastewater, Thirteenth Edition, 1971.

Calibration Points

The ORP measuring system shall be calibrated at two points using buffer solutions containing quinhydrone and having nominal values of 4 and 7 pH. The predictable potential of these solutions is a function of the temperature and the type of reference electrode used. For example:

Quinhydrone electrode to saturated calomel electrode potentials $E = 0.4529 - (0.000198322 T^{\circ}$ Abs.$)$ pH.

	Volts	Volts	Volts
pH	15°C	20°C	25°C
1.0	+0.396	+0.395	+0.394
4.0	+0.255	+0.221	+0.217
7.0	+0.053	+0.046	+0.040

When an Ag-Ag Cl reference electrode is used, 0.046 volts should be added to the values listed above. (E Ag. Ag Cl = E calomel +0.046).

SYSTEM MAINTENANCE

The criteria and recommended methods set forth in this document are intended to ensure use of reliable monitoring instruments capable of generating water-quality data that will meet acceptable levels of accuracy. However, the accuracy of field data depends not only upon the representativeness of the sample, the system performance (calibrated accuracy, transient response, stability and temperature compensation) and the method of calibration as outlined under sections entitled Sample, System Performance and System Calibration, but also upon the maintenance of the system. Preventive maintenance on a regularly scheduled basis for the intake system and the measuring system and sensors is necessary if a monitor is to operate within its system performance capabilities.

Intake System Maintenance

Routine cleaning of the intake system is essential, with frequency depending upon local conditions. Manual backflushing should be included on a scheduled maintenance program if an automatic backflushing feature is not included in the system design. It is important that the intake screening be kept free of debris. The manufacturer's recommended maintenance procedure should be followed for the pump, and installation must be sure that it can be easily removed for maintenance, repair, or replacement.

Sensor and Measuring System Maintenance

To maintain sensor performance and to ensure measuring system stability at an acceptable level, close surveillance and frequent servicing are required. It is important that sensor contamination be kept to a minimum and that frequent calibration checks be made for all parameter measuring systems. Systems having temperature-compensating elements should be occasionally checked to see that these elements are functioning correctly. The calibration checks should be performed at a minimum of three widely spaced temperature points. Experience indicates a reasonable interval between maintenance visits to monitor field installations to be approximately one week. However, no set schedule can be specified because of varying local conditions. On such maintenance visits, the differences between reported and actual values of a parameter both before and after maintenance should be determined. This information will be invaluable in computing the finalized data.

From time to time, during different seasons and under different flow conditions, checks should be made to determine that degradation of the sample between the system intake and the sensor sampling chamber does not exceed the limits outlined in the section on degradation.

RECOMMENDATIONS

Sensors now in use for measuring water-quality parameters are being continually improved to meet the demands for increased reliability and precision in automatic monitoring applications. In recognition of these improvements in the state-of-the-art and also in recognition of the frequently changing needs of water-quality management, any set of methods such as those set forth in this report cannot be considered as final. Therefore, it is recommended that there be periodic review of new developments in automatic water-quality monitoring so that the present methods can be revised accordingly.

It should be noted that the National Weather Service and others in private industry now have facilities for laboratory calibration of solar radiation sensors. However, additional study will be required before an acceptable procedure for field calibration of solar radiation sensors can be included in this report as a recommendation.

Metals
MET

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FOR

METALS IN WATER

MONITORING INSTRUMENTATION

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A. INTRODUCTION

This discussion encompasses metals in fresh, waste and saline waters, and particularly the effects of environmental factors on metal analysis. Topics covered include the sources, forms and toxic effects of metals in water, and discussion of the dynamics of metal transfer from insoluble to soluble phases. These topics are discussed from different viewpoints in various papers and books (Ref. 1-9).

The water pollution bill of October 1972 sets high standards for pollution control (Ref. 10) including decreased pollutant discharges. A discussion is included here on existing and potential methods for controlling discharges of metals which may be used to attain these standards. A recent example of decreased pollutant discharge is that of mercury compounds into various streams and rivers (Ref. 11, 12, 13).

A discussion is also included on health standards related to human uptake of metals, and national standards on the metal content in drinking and other waters. Standards are required because some metals in one form or another are detrimental to man. An immediate example is the number of lost lives and physical and mental impairments traceable to methylmercury and to mercury discharges, and the subsequent costs in terms of lost jobs in mercury-processing industries (Ref. 14).

Unfortunately, it is not always sufficient to reduce the content of metals in waste water because some metals which have been already discharged can be converted from the original innocuous, insoluble forms to soluble toxic forms, as happens with mercury (Ref. 12; 13; 14, p. 521). On this basis, control of toxic metals may have to include cleanup of previously discharged metals - cleaning by natural processes may take too long (Ref. 13; 14, p. 521).

1. Characteristics

Metals undergo a variety of chemical and biochemical reactions, including complexation, oxidation-reduction, precipitation by anions such as sulfide and carbonate, and conversion to organometallic compounds by microorganisms (Ref. 7, 12, 13). A change in pH may cause preferential precipitation of one form of an ionic redox couple such as Fe(III), as compared with the other form, Fe(II).

The mean concentration of a metal in fresh waters is usually below 1 ppm with the exception of some Group I and II metals which can be in the ppm range (Ref. 1). Polluted waters, effluents, estuarine water and bottom sediments and sludges may have much more dissolved or suspended metal as a constituent.

The range and frequency of detection of some trace elements in U.S. waters are shown in Tables A-1 to A-3 (Ref. 15). These tables contain analytical data on dissolved metals obtained from October 1, 1962 to September 30, 1967. The data in Table A-1 show that boron, barium and strontium were found most frequently (98-99.6% of all samples). The toxic metals, Cd, As, Be, and Ag occurred in less than 7% of the samples. (The term "positive" as used in Tables A-1, A-2 and A-3 refers to concentrations above the detection limit of the analytical procedure). The data are shown further in Tables A-2 and A-3 according to geographical locations. Permissible levels established by the USPHS Drinking Water Standards for public water supplies were exceeded in only isolated samples. The range and median concentrations of selected metals in drinking water can be found in the appropriate section for each metal in Standard Methods, 13th edition (Ref. 1). Water Quality Criteria (Ref. 2) also lists some figures for metal concentrations in water.

TABLE A-1

Summary of Trace Elements in Waters of the United States (from Ref. 16).*

Element	Frequency Of Detection, %	No. of Positive Occurrences	Observed Positive Values μg/l		
			Min.	Max.	Mean
Zinc	76.5	1207	2	1183	64
Cadmium	2.5	40	1	120	9.5
Arsenic	5.5	87	5	336	64
Boron	98.0	1546	1	5000	101
Phosphorus	47.4	747	2	5040	120
Iron	75.6	1192	1	4600	52
Molybdenum	32.7	516	2	1500	56
Manganese	51.4	810	0.3	3230	58
Aluminum†	31.2	456	1	2760	74
Beryllium	5.4	85	0.01	1.22	0.19
Copper	74.4	1173	1	280	15
Silver	6.6	104	0.1	38	2.6
Nickel	16.2	256	1	130	19
Cobalt	2.8	44	1	48	17
Lead	19.3	305	2	140	23
Chromium	24.5	386	1	112	9.7
Vanadium	3.4	54	2	300	40
Barium	99.4	1568	2	340	43
Strontium	99.6	1571	3	5000	217

*1,577 Samples (Oct. 1, 1962 - Sept. 30, 1967)
†1,464 Aluminum Analyses

2. Forms

The forms of metals in an aquatic environment include dissolved ions, particulates, colloids, organometallics and any insoluble compounds which lie on the bottom of polluted waters (Ref. 3, 6). Metals do not necessarily remain in one form, but instead can be converted from one form to another depending on the conditions. For example, iron can be found in the solid phase as an oxide or sulfide, in the aqueous phase as Fe(III) and Fe(II); Hg(II) is likely found as $Hg(OH)_2$, HgClOH, $HgCl_2$ in natural water systems (Ref. 16); while chromium may exist as cationic Cr(III) and anionic Cr(VI).

TABLE A-2.

Percent Frequency of Detection for Trace Metals by Basin (from Ref. 15)

	Northeast	North Atlantic	Southeast	Tennessee River	Ohio River	Lake Erie	Upper Mississippi	Western Great Lakes	Missouri River	Southwest – Lower Mississippi	Colorado River	Western Gulf	Pacific Northwest	California	Great Basin	Alaska
Zn	95.6	94.7	96.7	73.5	81.8	87.3	70.5	90.9	53.0	62.6	45.	48.9	90.1	72.4	68.4	83.3
Cd	4.4	7.6	1.1	0	2.9	8.5	1.8	3.0	0	0	1	2.1	2.5	0	5.3	0
As	5.5	7.6	8.8	1.5	8.3	4.3	7.1	4.5	2.0	1.3	2	4.3	8.6	0	5.3	16.7
B	100.	99.4	94.5	100.	99.2	100.	98.2	100.	97.3	99.4	98.	97.9	93.8	96.5	94.7	100.
P	60.4	55.6	51.6	39.7	48.8	53.2	77.7	48.5	39.5	30.3	22	23.4	52.5	62.1	26.3	55.6
Fe	87.9	78.9	98.9	83.8	68.6	66.0	80.4	78.8	66.0	80.0	59	70.2	80.2	93.1	73.7	94.4
Mo	13.2	32.7	18.7	38.2	28.1	27.7	68.8	51.5	32.0	20.0	37	10.6	38.9	37.9	57.9	27.8
Mn	50.5	48.5	72.5	57.4	58.7	61.7	61.6	56.1	40.8	34.8	39	38.3	51.2	44.8	57.9	61.1
Al	67.0	30.4	71.4	47.1	21.5	21.3	19.6	42.4	11.6	19.4	14	21.3	30.2	17.2	15.8	27.8
Be	1.1	23.4	1.1	1.5	14.1	6.4	0	1.5	2.0	0	0	0	0.6	0	0	0
Cu	97.8	92.3	95.6	91.2	72.3	50.4	80.4	97.0	49.7	63.9	33.	40.4	87.0	69.0	73.7	94.4
Ag	14.3	5.3	5.5	0	5.4	6.4	5.4	9.1	4.1	4.5	18.	4.3	8.6	0	5.3	5.6
Ni	22.0	28.1	20.9	8.8	25.2	53.2	15.2	9.1	2.0	9.7	8.	2.1	10.5	13.8	15.8	11.1
Co	2.2	1.2	1.1	0	9.9	4.3	0.9	3.0	0.7	0.7	2.	0	3.7	0	0	0
Pb	36.3	22.2	12.1	35.3	18.6	27.7	24.1	40.9	3.4	9.7	15.	2.1	22.8	6.9	21.1	38.9
Cr	56.0	21.1	40.7	47.1	23.6	23.4	17.9	28.8	4.8	20.0	17.	6.4	32.7	20.7	10.5	22.2
V	4.4	3.5	1.1	0	3.7	4.3	0.9	0	1.4	3.9	9.	2.1	6.2	6.9	0	5.6
Ba	100.	100.	100.	100.	100.	100.	100.	100.	98.0	100.	100.	100.	100.	100.	94.7	100.
Sr	100.	100.	98.9	100.	100.	100.	100.	100.	99.3	98.7	100.	100.	99.4	96.5	94.7	100.

TABLE A-3.

Observed Mean Positive Trace Metal Values by Basin, μg/l (from Ref. 15)

	Northeast	North Atlantic	Southeast	Tennessee River	Ohio River	Lake Erie	Upper Mississippi	Western Great Lakes	Missouri River	Southwest – Lower Mississippi	Colorado River	Western Gulf	Pacific Northwest	California	Great Basin	Alaska
Zn	96	49	52	28	81	205	45	24	39	85	51	92	40	16	44	28
Cd	5	3	5	–	7	50	6	5	–	–	2	10	5	–	1	–
As	34	47	35	50	66	308	69	37	123	91	53	22	68	–	20	34
B	32	42	29	24	67	210	105	19	154	131	179	289	30	143	84	28
P	44	48	43	42	130	153	243	31	353	81	121	173	47	83	37	40
Fe	51	19	120	37	28	35	35	22	37	69	40	173	32	46	70	25
Mo	25	33	15	25	70	68	88	28	83	95	130	24	30	45	145	17
Mn	3.5	2.7	2.8	3.7	232	138	9.8	2.3	13.8	9.0	12	10	2.8	2.8	7.8	18
Al	28	22	117	30	141	56	18	17	213	68	50	333	30	63	15	11
Be	0.02	0.12	0.05	0.16	0.28	0.17	–	0.05	0.23	–	–	–	0.02	–	–	–
Cu	15	17	14	11	23	11	14	7	17	19	10	11	9	12	12	9
Ag	1.9	0.9	0.4	–	2.1	5.3	3.4	1.4	1.2	4.3	5.8	3.5	0.9	–	0.3	1.1
Ni	8	8	4	4	31	56	15	10	5	17	12	3	10	10	4	5
Co	14	9	1	–	19	33	18	11	8	36	11		8	–	–	–
Pb	17	14	8	17	30	39	33	14	39	37	32	4	15	4	18	12
Cr	14	6	4	6	7	12	7	6	17	16	16	25	6	15	4	9
V	9	12	10	–	22	54	20	–	171	25	105	9	13	30	–	32
Ba	21	25	26	25	43	42	39	15	63	90	60	67	27	42	41	17
Sr	70	62	26	47	130	260	105	44	342	540	697	652	68	153	152	81

Water parameters which influence the form of a metal include pH, presence or absence of complexing anions such as F^-, and presence of a reducing substance such as Fe(II) or $SO_3^{=}$ (Ref. 3, 6). Some metals are converted by microscopic organisms in the aquatic environment from one form into another. Examples include the conversion of inorganic mercury into the lethal organometallic compound methylmercury by microorganisms (Ref. 7, 14) and selenium cycling (Ref. 17).

Significant amounts of metals in water can be present in the colloidal state either as the metal or as a colloidal metallic compound such as carbonate, silicate, or hydroxide (Ref. 3, 6). These colloidal forms are dispersed, and do not settle even on standing unless coagulated. They may be removed from the solution by means of a fine filter when it is desired to distinguish them from dissolved metals species (Ref. 3).

Metals may be present in more than one form in the same water sample. It is usual to convert all the forms into a single form by chemical steps such as acid digestion or oxidation-reduction, prior to the instrumental measurement. Premeasurement chemical reactions are discussed, when applicable, under each metal in Section D.

3. Sources

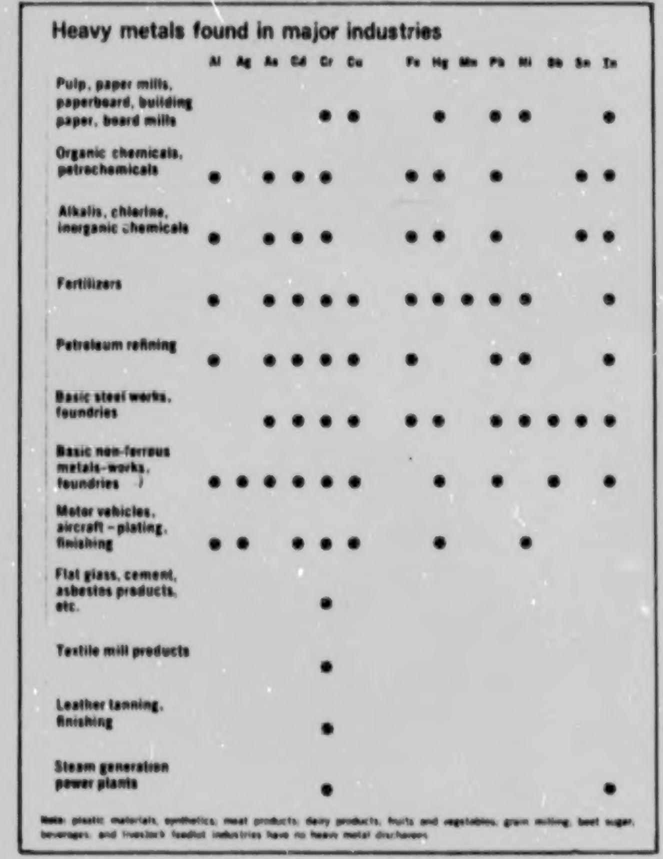
The aquatic environment receives metal contributions from a number of sources, including naturally occurring minerals, discharges from industrial, utility and municipal effluents (Ref. 8, 18), aerosols and particulates from the atmosphere (Ref. 7), and from the lithosphere (Ref. 3, 7). Natural waters contain traces of metals which are leached or dissolved from naturally occurring minerals (Ref. 18). Estuarine waters include metals which are present in the ocean (Ref. 6), and polluted and waste waters contain more or less of a particular metal depending on the nature of the discharge (Ref. 18). Some metal concentrations may be greater than expected under certain conditions, such as the increased lead content in drinking water traceable to lead used in old pipe or joint cementing compounds (Ref. 8, p. 196).

There has been an increase in the consumption of metals with known toxic properties. Over the 20 year period 1948-1968, U.S. consumption of cadmium increased from 3909 to 6664 tons, lead from 1,133,895 to 1,328,790 tons, mercury from 1758 to 2866 tons, and selenium from 419 to 762 tons (Ref. 8). The metal consumption for other selected metals is tabulated in Reference 8. In this connection, heavy metals associated with major industries are listed in Table A-4 (Ref. 18). The incidence of the metals found for each industry no doubt forms the basis for the industry-oriented metal analyses required for discharge permits by the EPA (Ref. 5).

TABLE A-4.

Heavy Metals Found in Major Industries

(from Ref. 18)



Heavy metals found in major industries

	Al	Ag	As	Cd	Cr	Cu	Fe	Hg	Mn	Pb	Ni	Sb	Sn	Zn
Pulp, paper mills, paperboard, building paper, board mills					●	●		●		●	●			●
Organic chemicals, petrochemicals	●		●	●	●		●	●		●			●	●
Alkalis, chlorine, inorganic chemicals	●		●	●	●		●	●		●			●	●
Fertilizers	●		●	●	●	●	●	●	●	●	●			●
Petroleum refining	●		●	●	●	●	●			●	●			●
Basic steel works, foundries			●	●	●	●	●	●		●	●	●	●	●
Basic non-ferrous metals-works, foundries	●	●	●	●	●	●		●		●		●		●
Motor vehicles, aircraft – plating, finishing	●	●		●	●	●		●			●			
Flat glass, cement, asbestos products, etc.					●									
Textile mill products					●									
Leather tanning, finishing					●									
Steam generation power plants					●									●

Note: plastic materials, synthetics, meat products, dairy products, fruits and vegetables, grain milling, beet sugar, beverages, and livestock feedlot industries have no heavy metal discharges

4. Control

Methods of controlling the metal content of water discharges include self-purification (Ref. 6), removal of metals by chemical or physical means, or controlling losses due to leakage (Ref. 14). Industries and utilities are making headway in reducing the metal content of their discharges by such methods as chemical precipitation, electrodeposition, cementation, solvent extraction, ultrafiltration for colloidal particles, ion exchange, and activated carbon absorption (Ref. 8, 18). Some of these techniques simply replace one metallic impurity with another, so that the overall approach must be examined to evaluate fully the various tradeoffs. For example, zinc dust is used in a cementation process to precipitate silver and gold from cyanide solutions, but zinc will be added to the water as complexed zinc ion according to the stoichiometric equation

$$2Au(CN)_2^- + Zn \rightarrow 2Au + Zn(CN)_4^{=}$$

One example of a working system is that applied to the manufacture of television picture tubes, in which lead and fluoride wastes are removed by treating the effluent with trisodium phosphate to precipitate lead phosphate. The treated waste with insoluble lead phosphate in suspension is then pumped into another tank where fluoride is precipitated as calcium fluoride. The precipitates of lead phosphate and calcium fluoride are allowed to settle to the bottom of other tanks, and the water drawn off. The sludge at the bottom of the tanks is periodically cleaned out and hauled to a land fill (Ref. 19).

5. Effects

The toxic metals which affect man include traces of As, Cr, Be, Cd, Pb, Hg, Se and larger quantities of other metals. Of these, Pb and Hg are most frequently the results of manmade pollution (Ref. 7, p. 338). The toxic effects vary according to the particular metal, the oxidation state of the metal, and the rate of excretion of the particular form of the metal (Ref. 2). Thus, As(V) is not considered as harmful as As(III), or arsenic metal (Ref. 20), lethal methylmercury is not excreted as rapidly as the less toxic inorganic forms of mercury (Ref. 12), Cr(VI) is considered more harmful than Cr(III) (Ref. 2, p. 164). Metals have other deleterious effects which indirectly affect man:

> "The presence of metals in domestic sewage, industrial effluents, and receiving streams is a matter of serious concern because the possible toxic properties of these materials may adversely affect sewage treatment systems or the biological systems of the receiving streams." (Ref. 1, p. 417)

Compounds of certain heavy metals including zinc, lead, copper, cadmium and mercury are toxic to fish, while toxicity caused by a mixture of two heavy metals may be enhanced due to a synergistic effect (Ref. 6, p. 307). The effects of metallic and other pollutants on selected fish form the basis of bioassay methods which are used to evaluate the toxicity of metals (Ref. 1, 6). Results of the bioassay can be used to "judge compliance with water quality standards established by water pollution control authorities." (Ref. 1, p. 562). Test results obtained from some metals in various forms on various species of fish are given in Water Quality Criteria, by McKee and Wolf.

Specific effects on man and the aquatic biota differ from metal to metal, and are discussed in the individual section for each metal.

6. National Water Quality Standards for Metals

The Public Health Service has published guidelines for drinking water which include recommended limits for several metals. The guidelines have been periodically reissued over the past fifty years to reflect any changes in recommended limits, and to include metals not previously included. The drinking water standards have been revised four times; a summary of the latest revision (1962) is given in the Introduction to this volume. A table of the changes in the standards is given in Reference 2; the EPA is expected to issue new standards in 1973.

Similar guidelines are also available for waters used by recreation; aquatic life, fish and wildlife; agricultural uses, and various industries (Ref. 2, 7). Additional details are included in the two references cited, and in the Introduction to this volume.

The EPA has published "Water Quality Standards Criteria Digest: A Compilation of Federal/State Criteria on Mercury and Heavy Metals." The compilation applies to drinking, recreational, fish and wildlife propagation, industrial and agricultural waters, and is available from the EPA.

7. National Discharge Standards for Metals

A permit program being prepared by EPA requires industries and municipalities to obtain discharge permits (Ref. 10). The permits will set firm targets - both interim and long term - for heavy metals as well as other pollutants. One provision requires permit holders "to continuously monitor their discharges into streams and lakes and to provide EPA with frequent reports. . . ."

B. MONITORING SYSTEMS

The number of steps or modules required for measuring metal contents depends to a large extent on the concentration of the metal. For example, pulse polarography, and atomic absorption methods can be applied directly to fresh water samples for metals including As, Cu, Fe, Mg, Zn, Ba, and Ca. Besides direct analysis, methods may use a premeasurement concentration step such as evaporation, ion-exchange, electrodeposition or precipitation. The different forms of the metal are usually converted by chemical reactions into a single form, which is subsequently measured. Thus, evaluation of methods for monitoring metals to determine the reliability must include the entire system, and not just the instrumental measurement.

1. Systems Concept

Systems for monitoring metals in water can be classified as either selective metal analyzers or simultaneous metal analyzers. In addition, they may be of the laboratory or field type.

Laboratory selective metal monitoring systems involve sampling on-site followed by laboratory analysis. Samples for metals analysis are usually collected in a bottle fabricated from polyethylene or a similar material to minimize adsorption or leaching metal ions from the sides of the container.

When data taking is not interrupted it is defined as being continuous. If data are recorded only periodically, a sampling process takes place, and the information is called sampled data. For example, an uninterrupted chart record of temperature is continuous, a reading every hour is sampled.

Field selective metal monitoring systems are usually portable and are of the type in which a sample stream is separated from the water and analyzed on-site. Data may be continuous or periodic, if an automatic analyzer is used.

Laboratory simultaneous metal monitoring systems utilize on-site sampling, with analysis performed in a laboratory away from the sampling site. More than one metal is determined simultaneously.

Field simultaneous monitoring systems are of the type in which a sample stream is separated from the water and analyzed on-site with an automatic analyzer. Data may be continuous or periodic.

2. Sampling

Sample collection and preparation are complicated for metals in water because of such factors as the low concentrations, frequent necessity of sampling from a moving stream, diversity of soluble forms and the presence of metals in the particulate state and in sediments. Samples taken for laboratory analysis are collected in a polyethylene or glass bottle to which concentrated hydrochloric or nitric acid is added "to a pH of approximately 3.5 in order to minimize precipitation and adsorption (of metals) on the walls of the container" (Ref. 1, 21). Samples for analysis of calcium and hardness do not require a preservative, and may be stored up to seven days before analysis. Samples intended for total or dissolved metals are preserved by addition of nitric acid, and may be held up to six months prior to analysis (Ref. 21).

The importance of preservation is indicated by the results of the study on mercury losses from creek water during storage (Ref. 22). Losses ranged as high as 60% for a water sample without added preservative after only minutes of storage under ambient conditions in a polyethylene bottle.

Sample concentration methods include ion-exchange columns; copper, gold or silver grids; and 0.45 µm membrane filters for suspended metals analysis. The ion-exchange column can be used to concentrate trace quantities of anions or cations (Ref. 1, 23). Metals may exist in both cationic and anionic forms, so that both forms must be eluted from the column. Silver wire is used for the collection and concentration of soluble mercury (Ref. 24).

Tradeoff considerations related to different sampling procedures for laboratory and field monitoring systems include: (1) the laboratory sample usually contains acid added as a preservative; the field sample may not, (2) the time lapse between sampling and analysis is longer for laboratory monitoring. A significant time lapse may be undesirable. For example, real-time information is necessary for water quality surveillance within a time frame "which encompasses the instant of undesirable occurrence through an ensuing period of time when successful correction action is practical" (Ref. 4).

A sampler system which includes filtration measures dissolved metals. Such analytical data represents a lower limit for certain metals because the particulates filtered out can contain significant amounts of the metal being analyzed. This can be the case for elements such as iron, manganese, aluminum and lead, "as these elements tend to precipitate or be adsorbed by other suspended materials quite rapidly...." (Ref. 15, p. 27). On the one hand, one would expect drinking water purification processes to filter out solids, so that a better correlation may be expected between analysis of dissolved metals and the metal content of drinking water. On the other hand, a true picture of the metal content in a particular water sample will be obtained only by analyzing suspended solids and sediments as well (Ref. 15, p. 14).

Data showing analyses of suspended and dissolved metals from one set of water samples are shown in Table B-1 (Ref. 15, p. 14). Copper, barium and zinc occur with about the same frequency in both the 228 suspended fractions as in the 1577 dissolved samples. Iron, manganese, aluminum and barium occur with 93-100% frequency in the suspended fractions.

TABLE B-1.

Comparison of Suspended and Dissolved Trace Metals in Surface Waters (Ref. 15)

	Suspended Metals 228 samples			Dissolved Metals 1577 samples		
	No. Pos.	%F	$\bar{X}$, μg/l	No. Pos.	%F	$\bar{X}$, μg/l
Zn	146	64	62	1207	76.5	64
Cd	0	0	–	40	3	9.5
As	–	–	–	–	–	–
B	52	23	44*	1546	98	101
P	–	–	–	–	–	–
Fe	228	100	3000	1192	76	52
Mo	–	–	–	–	–	–
Mn	212	93	105	810	51	58
Al	221	97	3860	456	31	74
Be	40	18	0.34	85	5	0.19
Cu	141	62	26	1173	74	15
Ag	0	0	–	104	7	2.6
Ni	7	3	29	256	16	19
Co	0	0	–	44	3	17
Pb	5	2	120	305	19	23
Cr	18	8	30	386	25	9.7
V	0	0	–	54	3	40
Ba	216	95	38	1568	99	43
Sr	22	10	58	1571	100	217

*A single boron value of 5,500 μg/l was observed in one sample. If this value were included in the calculations, the mean suspended boron value would be 148 μg/l.

Descriptions of sampling systems are given in Standard Methods, Vol. 13 (Ref. 1), and Methods for Chemical Analysis of Water and Wastes, 1971 (Ref. 21). The subject is discussed by McKee and Wolf (Ref. 2), Mancy (Ref. 3), and in Water Quality Criteria (Ref. 9).

3. Calibration

Calibration can be one of two kinds: instrument and systems. Instrument calibration methods include impression of a known electrical signal at the inputs of the instrument, use of an optical filter, or introduction of a known concentration of the metal through a portion of the monitoring system. The true concentration of metals in water samples cannot be calculated if only the instrument is calibrated, because metal may be gained or lost in untested portions of the monitoring system. Calibration of the entire monitoring system is best accomplished by introducing known concentrations of the metal directly at the sampling stage.

Calibration methods generally include the categories: (1) calibration curves, (2) standard additions, and (3) internal standards.

A calibration curve is obtained by analyzing known concentrations of the metal in exactly the same way that the water samples will be analyzed. Use of the identical, or a similar sample, to minimize matrix effects is important. The instrumental readout is corrected for the blank, and plotted versus known metal concentration to obtain the calibration curve. Changes in room temperature, instrumental blank, or reagent purity affect this curve.

In the method of standard addition, small volumes (often several microliters) of a solution containing a known concentration of the metal are added to the sample prior to analysis. Any necessary volume correction is made to take into account dilution caused by addition of the standard, and the instrument readout is calculated for both the known and unknown metal concentrations. The fraction of the signal output related to the known concentration of the added metal is determined, and the concentration of the metal in the sample is calculated. The method depends on a linear relationship between concentration and signal output; a blank correction for background must be made. Two or more standard additions to yield final concentrations less than and greater than the metal level in the sample should be carried out to obtain reliable results.

In the internal standard method, the magnitude of the instrument readout due to the unknown is compared to the readout due to a "reference" element which is present in fixed concentration in both the samples and the standards. The ratios of the concentrations of the internal standard and known metal concentration are calculated instead of the absolute metal concentration. Small changes in room temperature or instrumental parameters are better tolerated with this method than the other two. This method is used in x-ray fluorescence, atomic absorption and emission spectrometric methods.

An example of improved results is shown by the data in Tables B-2 and B-3, and the plots in Figure B-1 (Ref. 25) in atomic absorption analysis.

Calibration standards for metal monitoring systems are obtainable in a variety of forms. The National Bureau of Standards Special Publication 260 (July 1970) and the Supplement (January 1972) lists over 650 certified standard reference materials. These include ferrous and non-ferrous alloys containing less than 1% of many metals. Other standards include orchard leaves, coal, and beef liver.

Requests for information should be addressed:

Office of Standard Reference Material
National Bureau of Standards
Washington, DC 20234

Caution is required in the use of standards because of the multiplicity of forms which may be present and not all of which may respond to the analytical method. Properly chosen pretreatment is essential in such cases.

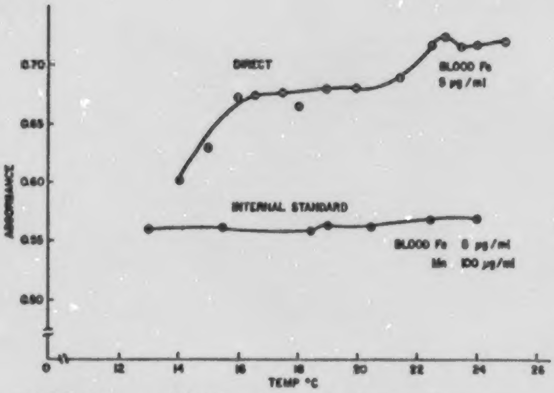


FIGURE B-1. Effect of sample temperature on absorbance of iron in dilute whole blood (Ref. 25).

TABLE B-2.

Elements Found Useful as Internal Standards (from Ref. 25)

Metal Determined	Internal Standard	Mode Studied[a]
Ca	Sr	A, E
Al	Cr	A, E
Fe	Au/Mn	A
Mn	Cd	A, E
Cu	Cd,Zn,Mn	A
Cd	Mn	A, E
Zn	Mn,Cd	A
Pb	Zn	A
Si	V,Cr	A
V	Cr	A
Ni	Cd	A, E
Cr	Mn	A
Mg	Cd	A
Co	Cd	A, E
Na	Li	A, E
K	Li	A, E
Au	Mn	A
Mo	Sn	A

[a] E = Emission, A = Absorption.

TABLE B-3.

Precision of Atomic Absorption Analyses Utilizing Internal Standards (from Ref. 25)

Metal Determined	Matrix	% R.S.D.[a]	
		Direct	Internal Standard
Ni	Stainless Steel	0.51	0.18
Mn	Aluminum Alloy	0.83	0.58
Fe	Aluminum Alloy	1.55	0.77
Mg	Aluminum Alloy	0.77	0.43
Ca	Cement	0.79	0.37
Fe	Whole Blood	0.49	0.21
Al	Cryolite	1.35	0.61
Au	Gold Alloy	0.85	0.22

[a] The statistics shown here are based on a series of 10 sequential analyses. The instrument was used in a normal laboratory mode with periodic confirmation of base-line calibration. The samples were prepared according to a normal chemical dissolution method as dictated by the matrices. R.S.D. is relative standard deviation.

4. Computerized Systems

Applications of computers to instrumentation for metals determination include digital readout, computerized data handling and control of analytical steps. Advantage of properly programmed computers includes improved accuracy due to removal of human error. Laborious manual measurements are unnecessary, calculations and control of environmental monitoring in a real-time mode are achievable.

Keller and Osteryoung applied systems computerization to the pulse polarographic method. A PDP-8/I computer manufactured by Digital Equipment Corp. was used for computing, measurement and control; Philbrick-Nexus SP 656 and P65AV operational and current amplifiers comprised the potentiostat (Ref. 26). See Figures B-2 and B-3. Response obtained on 4×10^{-8} $\underline{M}$ Cd (0.004 ppm) indicates usable data can be obtained at this level. A precision of 10% is indicated at 4×10^{-7} $\underline{M}$ Cd (0.04 ppm).

Clem and Goldsworthy built a novel instrument based on a digipotentiogratör for electroanalytical applications (Ref. 27); see Figures B-4 and B-5. The instrument controls the applied potential through pulsed injection or extraction of charges, while simultaneously serving as a current to digital converter. Currents can be measured with a precision of 0.01%. An outstanding feature is direct conversion of charge to a digital number thus simplifying data logging and reducing measurement errors. If current pulses are counted and summed in time, the digipotentiograter functions as an integrator.

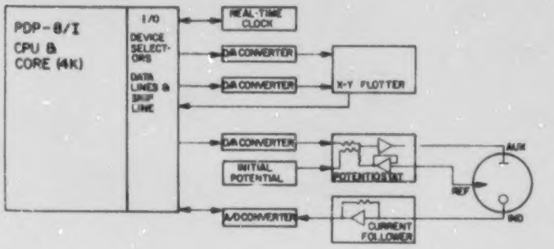
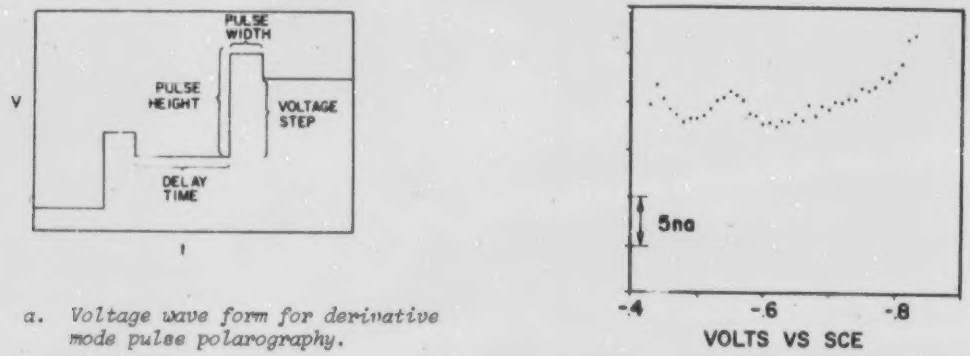


FIGURE B-2. *System block diagram (from Ref. 26).*

Considerable savings in weight, size, cost and power are achieved by direct conversion of charge transfer in an electrochemical reaction to a digital number. In the more usual electroanalytical instrumentation, the flow of charge is measured in analog fashion as the potential drop across a load resistor. Data logging may be on a pen-and-ink recorder, oscilloscope, or digitally without utilizing an A/D converter; see Figure B-4 and B-5.

Digitalization has advantages in remote sensing applications. Deleterious oscillations due to phase shifts are less likely than for analog systems. Because the detector output is immediately converted to numerical form, monitoring data can be easily and promptly transmitted to remote locations with higher signal to background ratios than obtained using the older instrumentation.

The cell reference electrode, "Ref," is connected through the noninverting input of a unity-gain impedance coupling amplifier to the



a. *Voltage wave form for derivative mode pulse polarography.*

b. *Derivative pulse polarogram of 4×10^{-8} $\underline{M}$ Cd^{2+}, 5×10^{-4} $\underline{M}$ KNO_3.*
20-cycle average without smoothing.
$A = 0.0414\ cm^2$. Pulse height = 50 mV.
Pulse width = 20 msec. Delay = 200 msec.

FIGURE B-3. *Signal input and resulting polarogram for derivative pulse polarography (from Ref. 26).*

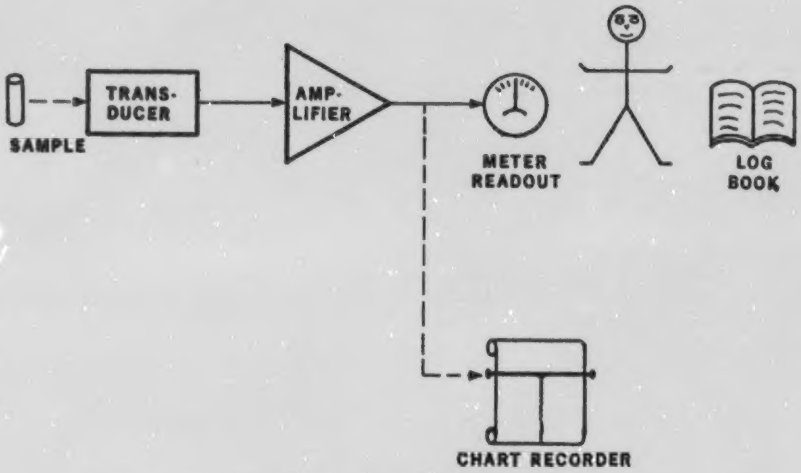


FIGURE B-4. Water-quality monitor with analog readout (from Ref. 29).

inputs of the two differential comparators. (Fig. 2, Ref. 27). The logical circuitry in turn senses the need for any rebalance current and controls the rate of pulses current to satisfy the cell current demands at the selected applied potential. Control of the potential of the working electrode may be obtained by applying the output signal of a low voltage power supply to the other input terminals of the differential comparator amplifier pair.

Polarographic and stripping voltammetric programs are available. The data can be logged onto magnetic tape for subsequent analysis with programs compatible with a Control Data Corp. 7600 computer. Magnetic tape data storage of the digitally recorded measurements permits the entire current-voltage sweep to be displayed after the analysis. The recorded data may be analyzed by expanding fullscale, after the fact, any portion of the sweep for visual inspection. Importantly, the data recorded on magnetic tape can be processed with a computer to compensate for background contributions and to integrate the peak areas.

The digital instrumentation was applied to determination of a mixture of 2.5 x 10^{-9} M Pb and 12 x 10^{-9} M Cu. Anodic stripping analysis was from a cell containing 250 µl saturated KCl and 13.4 µg Hg (as the nitrate) which were added to 15 ml of water. The cell was deaerated by nitrogen sparging. Amalgam accumulation time was 20 min. Discernable peaks for both Cu and Pb could be obtained by tenfold expansion of the recorded stripping trace. The peaks are barely discernable from background in the unexpanded trace.

The digipotentiograter is being applied

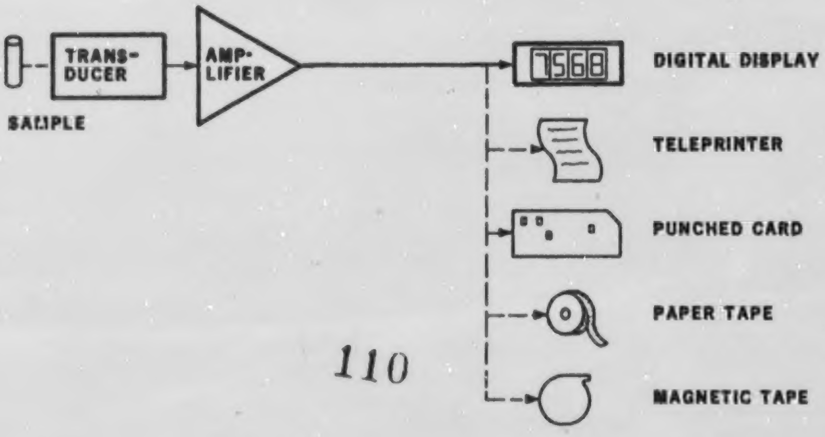


FIGURE B-5. Water-quality monitor with direct digital readout (from Ref. 29).

in an environmental study to determine lead in fresh waters. The instrument is admirably suited to this task; Pb in fresh waters has a mean value of about 140 ppb, and in drinking waters, about 20 ppb (Ref. 1, p. 196).

An IBM 1620 computer with a 40 k memory was used for data handling in DC arc spectrographic analysis (Ref. 28). The program developed includes calculations of emulsion calibration, background corrections, internal standard ratio calculations, electron pressure, arc temperature, and corrections for matrix effects. The computer used had limited storage capacity; the maximum number of lines measurements that can be processed at a single time is 140. This is usually more than adequate for measurements from a single plate. On a larger capacity machine, working curves for a number of elements can be stored to obtain thereby readout in terms of concentrations from the corrected line intensities.

A/D converters are commercially available for atomic and molecular absorption instruments. See the appropriate instrument notes.

Additional information on computerized instrumentation may be found in New Technologies, by Mack (Ref. 29) and "Digital Control Computers in Analytical Chemistry," by Frazer (Ref. 30).

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C. METALS IN WATER INSTRUMENTATION

Prior to 1940, most metals were analyzed using volumetric or gravimetric procedures. Since then, instrumental methods have achieved greater prominence because of increased sensitivity, selectivity, capability of simultaneous analysis, amenability of automation, and eventual lower cost per sample due, ie., to a decrease in turnaround time.

Instrumentation for monitoring metals in water is classified as either laboratory or field types. Manual samplers are used to collect samples which are later analyzed in the laboratory, while automatic samplers are able to collect and analyze the sample continuously on-site. Instrumentation may be classified further as either selective or simultaneous metal analyzers. Selective analyzers determine one metal at a time, although they may have multielement capability. Simultaneous analyzers measure more than one metal in the same sample at the same time. Selective and simultaneous analyzers may be either manual or automatic sampling.

Simultaneous analyzers are capable of measuring the concentrations of more than one metal in a sample during a single analysis. Most analyses are performed in the laboratory on manually obtained water samples. Instrumental methods include atomic emission spectroscopy, x-ray fluorescence, neutron activation analysis, anodic stripping, and spark source mass spectrometry.

With metal selective instrumentation, the analytical procedure is optimized for one metal; other metals either do not interfere, are removed, or are masked prior to measurement. Continuous analyzers such as those used for Hg, Cu, and Si fall into this category. Laboratory instrumentation includes UV-visible absorption and fluorescence, coulometry, chemiluminescence and atomic absorption. By far, the most widely used method has been atomic absorption.

Prior to analysis, samples may require pretreatment of the metal or matrix. Depending on the sample and the desired information, this might entail digestion of solids or organometallics, extraction, further preconcentrations, pH adjustment, or masking interferents.
For example, Cu, Fe, Mg, and Zn can be measured directly using atomic absorption spectrophotometry, but if particulate matter is present, the sample is treated with nitric acid and autoclaved prior to atomic absorption analysis.

Many instrumental methods are available for measuring the metal content of water. Some of them are summarized in order of increasing sensitivity in Table 1. In principle, all these methods can be used on a particular sample by bringing the metal concentration within the sensitivity limits by appropriate pretreatments such as dilution or precipitation. Undesirable features of pretreatment include increased likelihood of analyst error, metal loss or sample contamination, longer analysis time and need for highly purified chemical reagents. Individual instrumental methods for metals analysis follow; specific applications are given under each metal in Section D.

Table 1.

**Sensitivities of Instrumental Methods for Monitoring Metals in Water.*

Instrumental Method	Sensitivity,ppb (μg/l)
Polarography	100 - 1000
Molecular Absorption	100 - 1000
Atomic Absorption (Flame)	100 - 1000
Atomic Emission	100 - 1000
Square Wave Polarography	10 - 100
Sweep Voltammetry	10 - 100
Emission Spectroscopy (Arc)	10 - 100
X-Ray Fluorescence	10 - 100
Pulse Polarography	1 - 10
Molecular Fluorescence	1 - 10
Spark Source Mass Spectrometry	1 - 10
Anodic Stripping	0.1 - 10
Neutron Activation	0.1 - 10
Atomic Absorption (Flameless)	0.1 - 10
Chemiluminescence	0.1 - 10
Emission Spectroscopy (Plasma)	0.1 - 10

*For any method, the sensitivity will vary according to the particular metal.

C.1. CONTENTS FOR
ATOMIC SPECTROMETRY

	Mnemonic
1. Principle of Operation	
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a.1 Flameless Techniques	Atomic Spectrometry
b. Atomic Emission Spectrophotometry	
c. Atomic Fluorescence	
2. Applications	
3. Instrument Comparisons	
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5. References	
6. Table of Atomic Spectrometry Instrumentation	
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ATOMIC SPECTROMETRY

1. Principle of Operation

Atomic spectrometry includes three techniques: Atomic Absorption, Atomic Emission and Atomic Fluorescence. Light from a lamp containing the element to be measured is passed through a vapor containing atoms of the element. Some of the light is absorbed by the atoms. If the attenuation of the lamp's light intensity is measured, the method is called atomic absorption (AA). Hence, AA instruments measure the amount of light absorbed by elements as electrons are promoted to higher states. Conversly, atomic emission (AE) instruments measure the amount of light (photons) emitted by activated electrons as they fall back to lower energy states. Atomic fluorescence (AF) instruments measure the photons emitted at right angles to an incident light beam from a lamp containing the element to be measured.

a. Atomic Absorption Spectrophotometry

A special lamp containing the element of interest is used to emit a line spectrum of the element to be determined. The sample is injected into a flame, furnace, or other means of heating to produce free atoms in a vapor. Light from the lamp is absorbed by atoms of the element proportional to their concentration in the vapor. A filter (monochromator) usually isolates the wavelength of interest, and a photodetector measures the intensity of the lines. For double-beam optical systems this measurement is compared with the intensity of the original line spectrum emitted by the lamp. The results are usually converted and calibrated to read out directly in concentration values.

Atoms are capable of absorbing light in the ultraviolet and visible region by interacting with a photon to induce an electronic transition from the ground state to one of the excited states. The amount of light absorbed is related to the concentration of the absorbing atoms over a defined range by an exponential law: that is, over a concentration range the variation in absorbance (logarithm of the ratio of incident-to-transmitted intensity) is linear with concentration. This forms a basis for the quantitative application of atomic absorption to trace analysis. Atomic absorption is not normally used for qualitative analysis (i.e., to discover what is in the sample) but rather is a precise instrument intended for quantitative analysis (i.e., to determine the concentration of an element known to be in the sample).

Free atoms are necessary for atomic absorption; these are obtained only in the gas phase. The first requirement is therefore gasification of the element from the sample matrix. Methods used for gasification include aspiration of a sample solution into a flame, use of a graphite furnace, and chemical reduction in aqueous solution followed by air bubbling.

Flame atomic absorption is the common gasification technique using air-acetylene and nitrous oxide-acetylene mixtures as flame sources. The sample is aspirated as a "fine" mist into the flame, wherein it undergoes a series of reactions resulting in the formation of free atoms. The flame method is very inefficient and wasteful of sample; losses occur because most of the large drops in the mist are not converted to atoms in the flame, and the small drops suffer from a short residence time in the flame. Sensitivities vary according to the sample but are usually in the 5 - 2000 ppb range; occasionally a preconcentration step is needed (e.g., solvent extraction or evaporation). The cold vapor method for mercury is unusually sensitive, measurements below 1 ppb are not uncommon.

Atomic spectra have extremely narrow lines, usually only about 0.2 nm wide. Since "monochromatic" light from a conventional monochromator such as a hydrogen lamp covers a relatively wide band of wavelengths, no significant reduction of the incident light will be observed by the detector. Thus, hollow cathode tubes (composed of the analyzed metal) are used as the source of monochromatic radiation. In addition to the lines emitted by the metal vapor, there is a continuum from the inert carrier gas (Ar, He) which is focused on the exit slit detector and may swamp out the desired signal. To overcome this background, a monochromator is placed in the system to disperse unwanted lines so that they do not fall on the detector. The monochromator is often a grating, mounted in the Czerny-Turner or Ebert mode. A schematic diagram is shown in Figure 1 for a typical single beam spectrophotometer with a Czerny-Turner monochromator.

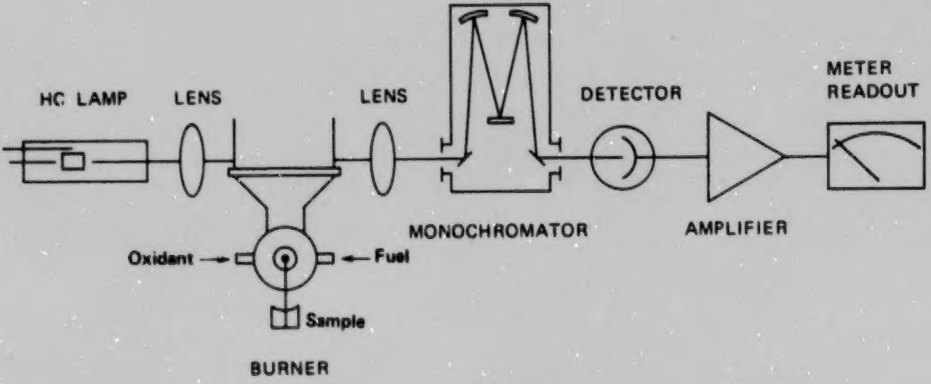

HC LAMP
LENS
LENS
MONOCHROMATOR
DETECTOR
METER
READOUT
AMPLIFIER
Oxidant
Fuel
Sample
BURNER

FIGURE 1. Jarrell-Ash Dial Atom II. Czerny-Turner mounting; single beam spectrophotometer; analog data display (Ref. 15)

Mirror optical systems are considered to be superior to lens systems since they can spread the light out more evenly across a grating. This allows greater sensitivity near the edges of the wavelength region allowed by the optics. Also, optically flat mirrors are less expensive and perhaps more reproducible than ground lenses. Hence, measurements performed using the same calibrated samples should produce better comparisons among several different mirror systems, than would be the case for several different lens systems.

In double beam optical systems, the ratio of a beam which passes through the sample to a reference beam is optically determined. A single phototube is alternately used to measure the two signals. Using one photodetector is superior to using two detectors since two separate detectors are never identical over long periods of time and wide temperature ranges.

A schematic for a typical double beam AA spectrophotometer is shown in Figure 2. A pulsed power supply drives a hollow cathode lamp. The light beam from the lamp is alternately passed through the flame and around the flame (reference beam). The diffraction grating filters the light and selects the spectrum segments transmitted to the photomultiplier detector. The electrical output of the photomultiplier is processed to drive a digital readout, a teletype, a printer, or a strip chart.

A rotating mirror is used in some double beam systems to direct the light beam alternately through the flame (sample beam) and past the flame (reference beam). A half silvered mirror is used to recombine the beams and transmit the signals to the monochromator and detector. A typical optical path for a mechanically chopped double beam system is given in Figure 3 (Ref. 3). The

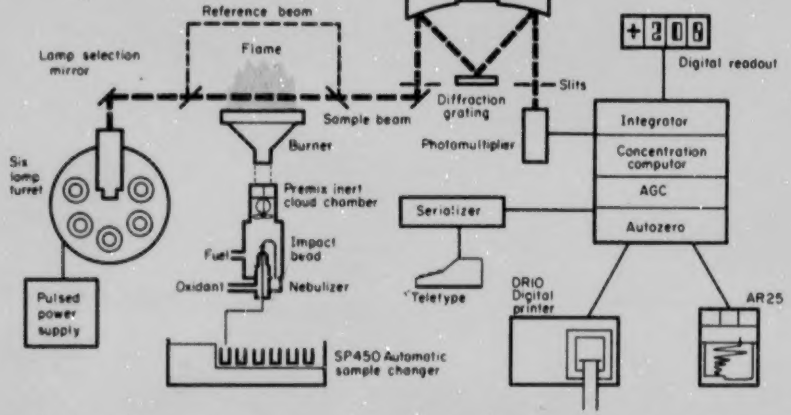

Reference beam
Flame
Lamp selection mirror
Sample beam
Diffraction grating
Slits
+208
Digital readout
Integrator
Concentration computor
AGC
Autozero
Photomultiplier
Burner
Six lamp turret
Premix inert cloud chamber
Impact bead
Fuel
Oxidant
Nebulizer
Serializer
Teletype
Pulsed power supply
DRIO Digital printer
AR25
SP450 Automatic sample changer

FIGURE 2. Schematic diagram for the Unicam SP 1900, a double beam spectrophotometer. (Ref. 16)

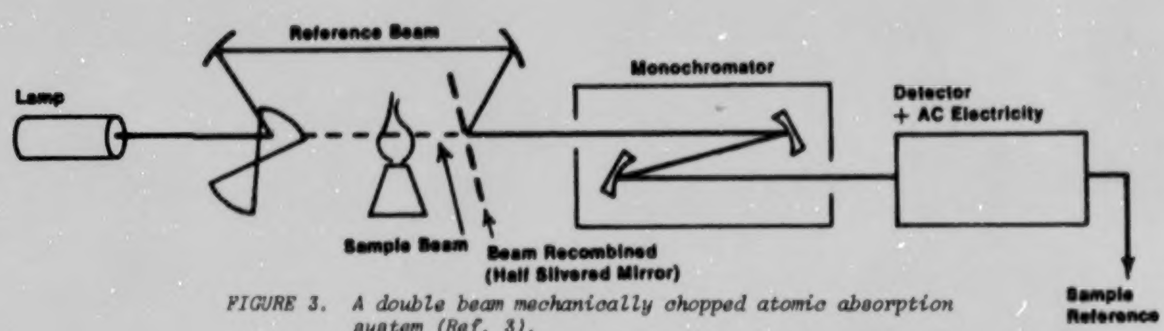


FIGURE 3. A double beam mechanically chopped atomic absorption system (Ref. 3).

double beam ratio system compensates for drift in lamp intensity, detector sensitivity, and electronic gain. Lower detection limits, greater precision, and little or no change in the method of operation are obtained. A mechanically chopped light beam is considered superior to an electrically pulsed hollow cathode lamp since the latter approach may tend to shorten lamp life.

A premix burner improves the repeatability of using the flame technique. However, a large fraction (about 90%) of the sample flows down the drain without ever reaching the flame. The sample that does reach the flame stays in the optical beam path for only small fractions of a second, and the premix burner is limited to use with solutions or very fine suspensions (Ref. 4).

A major advantage of the atomic absorption technique is the exceptionally wide range over which measurements can be made. Typical commercial instruments cover from ppb's to ppm's. This wide range allows the technique to be used to analyze metal atoms adsorbed on particulates in air.

a.1 Flameless Techniques

Research continues toward eliminating the flame and replacing it with an alternative means for converting the sample to an atomic state. One major motivation for this work is that only about 2 to 8% of the sample is reduced to elemental form by a flame. Not only is this low efficiency wasteful of sample material, but a small (2%) variation in "atomization" conversion efficiency (say from 2 to 4%) is a factor of two change in the amount of sample in an atomic state which can affect the measurement. Improvements in the fuel control, oxidant control, and sample preparation and introduction have provided a reasonably stable, uniform flame. Unfortunately, the reluctance of some personnel to use a flame, the need to have a volatile fuel in the laboratory, venting requirements, and temperature variations across a flame limit the extent of the flame technique.

The furnace supplements the flame. It can reduce as much as 100% of the sample to elemental form, thereby extending the detection limit by a factor of 10 to 1000 (Ref. 12). Direct analyses of liquid samples are feasible, and premeasurement concentrations can be avoided for some elements thus simplifying procedures. A graphite oven is shown in Figure 4 and detection limits are shown in Table 1 for a furnace and a flame (Ref. 4).

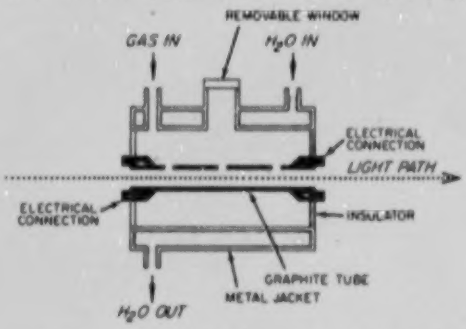


FIGURE 4. Cross section of the HGA-2000 (Perkin-Elmer) graphite oven (Ref. 4).

Flameless techniques generally produce an absorbance peak of relatively short time duration, as compared to the "steady" signal obtained from a flame. Therefore peak readers, automatic zero circuits, and circuits which automatically determine the concentration are needed. A definitive comparison should be performed between pulse height and pulse area measurements for identical calibration samples. When such a task is undertaken for many samples, then one should also perform further studies

TABLE 1.

Typical Detection Limits (From Ref. 4)

	Graphite Furnace		Flame
	Grams $\times 10^{-2}$	µg/liter	µg/liter
Al	3	0.03	20
Sb	20	0.2	40
Bi	10	0.1	25
Cd	0.1	0.001	0.2
Cr	5	0.05	3
Co	4	0.04	10
Cu	1	0.01	1
Au	8	0.08	10
Fe	3	0.03	5
Pb	6	0.06	10
Mn	1	0.01	2
Ni	10	0.1	2
Si	8	0.08	20
Ag	0.25	0.0025	2
Tl	14	0.14	30
Zn	0.06	0.0006	1

of base line drift, integration period lengths, accuracy, precision, and interferences to establish calibration reference points.

Another source of atoms is the cold vapor flameless technique which is widely used to monitor mercury levels in liquids (Ref. 7). The system utilizes chemical reactions which convert all forms of mercury into mercuric form, which is subsequently reduced to mercury metal. The mercury is swept out of the aqueous phase by a gas stream and into the absorption cell where the measurement takes place. The technique is applicable to Hg analyses at the low ppb level.

Vapor methods have been similarly applied to As, Se, and Sb by chemically converting each element to the corresponding volatile hydrides. A gas stream sweeps the vapor into an argon-hydrogen entrained air flame where the concentration is measured. Sensitivities for these vapor techniques are given in Table 2.

TABLE 2.

Sensitivities for Hg, As, Se, Sb Using Vapor Techniques (Ref. 8)

Element	Sensitivity, ng
Hg	2
As	4
Sb	50
Se	5

An ultrasonic nebulizer increases the sensitivity by reducing the size of the droplets which form the aspirated mist. Benefits of smaller drop size include both: (1) increased delivery efficiency from a decrease in condensation probability, and (2) increased atomization efficiency because less time is required for evaporation of the droplet. An enhanced sensitivity for Ag, Cd, Mg, and Zn was found for an ultrasonic nebulizer (Ref. 9). Data are shown in Table 3.

TABLE 3.

Enhanced Detections with Ultrasonic Nebulization (Ref. 9)

	Detection Limit, ppb	
	Without Ultrasonic	With Ultrasonic
Ag	20	5
Cd	8	3
Mg	2	1
Pb	20	30
Zn	6	2

Although the principle appears promising, a few disadvantages are also introduced by ultrasonic nebulizers. Some considerations which need further study are the interferences which may also be released during sample preparation, dissolved solids in the sample, repeatability, and any vibrational effect on the optical alignment.

b. Atomic Emission Spectrophotometry

Atomic emission spectrophotometry relies on the principle that elements emit photons with characteristic wavelengths when outer electrons fall into inner shells. Electrons must first be pumped or excited to outer shells by heating to provide both a supply of activated electrons and a partially vacant shell at a lower energy level. The intensity of emission at a characteristic wavelength is proportional to the amount of the respective element over a specified concentration range. The intensity may be measured using a densitometer to compare line blackenings on a photographic plate, or by direct readers which use photoelectric devices. The intensity of emission is related to concentration by comparing the results for a sample to data from known calibration samples.

The minimum detectable concentration is limited by many of the same factors that limit the use of atomic absorption. Complete sample atomization and the length of time that the sample is in the field of view of the detector both have major influence. Reabsorption of emitted photons, dispersion by other atoms, temperature gradients, and interferences from other substances may also affect the measurement.

In addition, the effect of fractional solid angle must be considered. A population of electrons changing states does not emit radiation in a focussed or uni-directional fashion, but rather somewhat uniformly in all directions. However, the detector usually has a limited field of view, less than a complete sphere surrounding the sample volume.

A disadvantage of atomic emission is the limitation to elements: compounds must be decomposed before they can be measured. Matrix and media effects are similar to those in atomic absorption and some premeasurement concentrations may be required.

A major advantage of atomic emission is that several elements can be analyzed simultaneously.

The steps involved in performing a measurement using atomic emission were described in Reference 1, page 3, as follows:

> "The sample to be analyzed is usually converted to liquid form, for instance as a solution in water. This solution is aspirated into a pneumatic nebulizer and dispersed as a fine spray of droplets. This spray is carried into the flame by the gas that operates the nebulizer. The flame is produced on a burner by combustion of a fuel gas (e.g., C_2H_2) with an oxidant gas (e.g., air). Under the influence of the high temperature of the flame the solvent evaporates and the remaining dry aerosol particles volatilize from the solid or molten state into the gaseous state. In this state the element to be analyzed (e.g., Ca) may be present as free neutral atoms (Ca) or molecules (CaO), or as positive ions ($CaOH^+$ and Ca^+). Whereas desolvation and volatilization are irreversible processes, reversible reactions and processes usually set up a certain balance between the atomic, molecular, and ionic metal species in the gaseous state.
>
> "These sample transformations and the related processes are summarized in Fig. 5. The successive stages are denoted

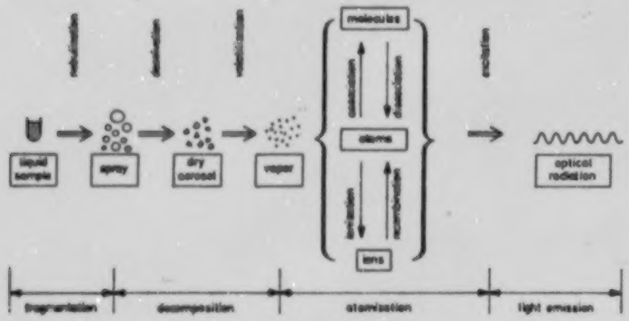


FIGURE 5. Transformation of a liquid sample into an optically radiating vapour in emission flame photometry. The processes acting in the different stages of this transformation are indicated (Ref. 1).

by: fragmentation, decomposition, and atomization (i.e., formation of free atoms by molecular dissociation or ion recombination, and vice versa). In the vapour state the metal species are excited whereupon they may emit atomic or ionic spectral lines, or molecular spectral bands in the near infra-red, visible, or ultraviolet parts of the spectrum. The flame temperature plays an important role in the excitation and usually in the atomizations of the sample. Occasionally it is also an important factor in the decomposition of the sample.

"A suitable line or band of the element is selected from the flame spectrum by a spectral filter or monochromator, and it is detected by means of a photocell (e.g., barrier-layer cell or photomultiplier tube). The photocurrent of the cell is often amplified by electronic means before it is measured by a read-out meter or recorder."

Various means are available to perform the atomization stage of the transformation. For example, a plasma may be used as an excitation source to overcome the lack of sensitivity of a conventional emission spectrophotometer. Detection limits are shown in Table 4 for metals analyzed using an induction coupled plasma source (Ref. 13,14).

A plasma is any luminous gas in which a significant fraction (>1%) of its atoms or molecules are ionized. Furthermore, plasmas may be generated by noncombustion techniques such as electrical means, and electrodes may or may not be essential. The ionized gas of a plasma can interact with magnetic fields by proper coupling. Such interactions can impart additional engeries to excite and ionize atomic and molecular species, or provide better control over the discharge.

Fassel at the Ames AEC laboratory utilizes electrodeless Joule heating caused by the magnetic field inside an inductor coil to generate a plasma. High frequency currents (4 to 50 MHz) flow in the inductor and thereby generating an oscillating magnetic field. These magnetic fields induce an eddy current which meets resistance and results in Joule (I^2R) heating of the plasma. The heating causes additional ionization. Electrons are "seeded" by means of a Tesla coil to initiate the plasma. The plasma is maintained by the eddy current induced Joule heating (Figure 6), and is equivalent to a very hot gas.

TABLE 4.

Detection Limits of Metals Using Plasma Excitation Emission Spectroscopy (Induction Coupled) (Ref. 13,14)

	Detection Limit, ppb	
Element	Fassel	Boumans, deBoer
Ag	20	
Al	2	0.2
As	100	360
B	30	80
Ba	0.1	0.02
Be	10	0.4
Ca	3	0.02
Cd	30	3
Co	3	
	1	0.3
Cu	1	0.1
Ce		2
Fe	5	0.3
Ga		0.6
Ge		4
Hg	200	1
La		0.4
Li		0.3
Mg	5	0.05-0.2
Mn	3	0.06
Mo	5	0.2
Na	<0.2	0.3
Ni	0.6	0.4
P	100	70
Pb	8	2
Pd		2
Se	30	
Si	300	
Sn		30
Sr	0.02	
Ti		0.2
U	30	
V	6	0.2
W		1
Y		0.06
Yb		0.04
Zn	9	16
Zr		0.4

Temperatures reach 9000-10,000°K, so that atomization is almost complete. Matrix effects such as selective volatization are thus minimized. Atoms have a long residence time within the plasma, leading to a higher excitation probability and more intense read-out. This high residence time accounts in part for the increased sensitivity.

Plasmas may also be generated with radiowave and microwave frequency excitation. Methods applied to mercury analysis have the advantage over atomic absorption in that organic substances which absorb at 253.7 nm interfere in atomic absorption, but not in plasma emission.

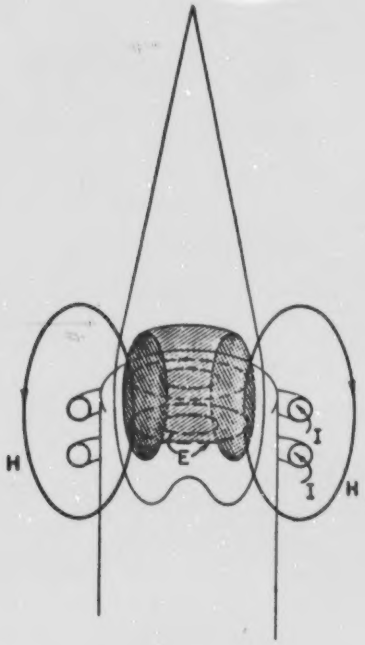


FIGURE 6. Schematic representative of induction-coupled plasma showing the magnetic field H produced by current I in the induction coil, and the eddy current E which is induced in the plasma (cross hatched area) (Ref. 13).

The SpectraSpan 101 utilizes plasma excitation in DC arc emission mode for metals analysis. Samples may be in the gas, liquid or solid phase. The monochromator (Figure 7) utilizes a grating/prism for line separations.

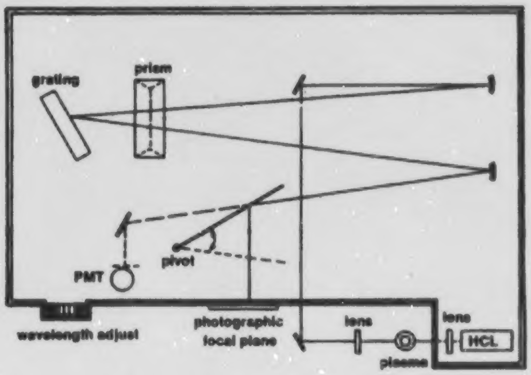
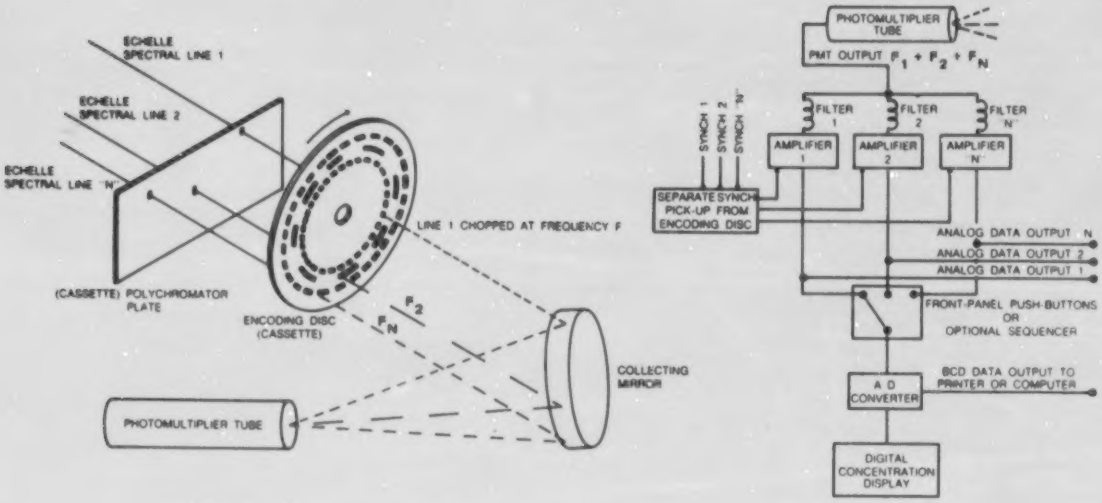


FIGURE 7. SpectraSpan 101. (Ref. 17)

In the SpectraSpan Model 210, the spectrum is projected to a polychromator/encoding cassette (Figure 8). The polychromator plate has ten exit slits, each located for a spectral line of one of ten elements being analyzed in the sample. The Lines are focused by the slits onto a rotating encoding disc where they are modulated (chopped) at frequencies determined in part by the radial distance on the disc. All of the modulated light is collected by a mirror and converted to an electrical signal. The amplified composite output from the photomultiplier tube passes through filters corresponding to the encoding frequencies, and each output fed to one of ten lock-in ampliers. The signal intensity is a function of the metal concentration, and can be displayed on a multi-pen-strip-chart recorder. The signals can also be switched to an internal analog-to-digital converter for digital display, printing, or computer storage.

Cassettes are available for any combination of up to ten metals. The cassettes may be custom made, or are available for common group elements found in biomedical materials.

Boumans and deBoer applied induction-coupled argon plasma to single and multi-element demonstration solutions (Ref.14). Detection limits for single elements are compared with those obtained by Fassel. (See Table 4). For simultan-


ECHELLE SPECTRAL LINE 1
ECHELLE SPECTRAL LINE 2
ECHELLE SPECTRAL LINE "N"
(CASSETTE) POLYCHROMATOR PLATE
ENCODING DISC (CASSETTE)
LINE 1 CHOPPED AT FREQUENCY F
F2
FN
COLLECTING MIRROR
PHOTOMULTIPLIER TUBE
PHOTOMULTIPLIER TUBE
PMT OUTPUT F1 + F2 + FN
SYNCH 1
SYNCH 2
SYNCH "N"
FILTER 1
FILTER 2
FILTER "N"
AMPLIFIER 1
AMPLIFIER 2
AMPLIFIER "N"
SEPARATE SYNCH PICK-UP FROM ENCODING DISC
ANALOG DATA OUTPUT N
ANALOG DATA OUTPUT 2
ANALOG DATA OUTPUT 1
FRONT-PANEL PUSH-BUTTONS OR OPTIONAL SEQUENCER
A D CONVERTER
BCD DATA OUTPUT TO PRINTER OR COMPUTER
DIGITAL CONCENTRATION DISPLAY

SPECTRAL ENCODING

SIGNAL PROCESSING

FIGURE 8. SpectraSpan 210 Encoding and signal processing schematics. (Ref. 17)

eous metals analysis. optimum excitation conditions can differ for the separate elements. Boumans and deBoer are studying simultaneous metals analysis using plasma excitation.

Refinements and improvements of instrumentation based on the atomic emission principle are now under development.

c. Atomic Fluorescence

Atomic fluorescence (AF) may be considered as a combination of atomic absorption (AA) and atomic emission (AE). AA instruments measure the amount of light absorbed by elements as electrons are promoted to higher states. AE instruments measure the amount of light emitted by activated electrons as they fall back to lower energy states. AF uses the hollow cathode light sources of AA for promoting electrons to higher states and the emission processes of AE. One fundamental difference of AF from AA is that the detector is placed at a right angle to the light beam emitted by the lamp as shown in Figure 9. (Ref. 3, page 225).

A primary purpose of this arrangement is to improve the signal to background ratio. However, the total amount of light collected by the detector is also significantly less, hence a very sensitive detector is required. One solution to this problem is to use a brighter lamp to excite more transitions. Unfortunately the scatter (interference) increases as the intensity of the light source increases. The requirements of low background and flame noise are far more important in AF than in AA. In AA the flame background is generally quite small compared with the source line intensity.

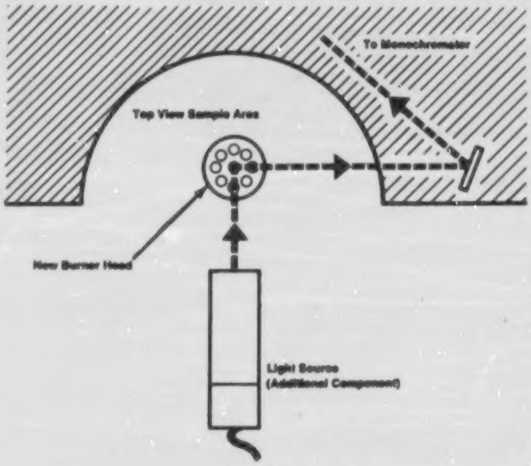

To Monochromator
Top View Sample Area
New Burner Head
Light Source
(Additional Component)

FIGURE 9. Emission from hollow cathode lamp causes samples to fluoresce proportional to concentration of desired element. (Ref. 3)

Reference 10 contains a discussion of the effect of using various fuels and hence changing the flame temperature, which in turn affects the success of atomization of elements. Reference 10 also provides a list of 68 references beginning with Winefordner and Vickers' work published in Anal. Chem. Vol. 36, No. 161, 1964. Cresser and Keliher state, "although the use of acetylene flames may lead to some loss of sensitivity, their use is recommended for analysis of a wide range of real samples since the extent of chemical interferences is considerably reduced."

It appears that although AF has the advantages of both AA and AE it also has the combination of their disadvantages. It is not clear at present if AF will gain wide acceptability in the near future. At present (Dec. 1973) it is our opinion that AF does not have a clear superiority for any particular element. However, the prospect of performing simultaneous quantitative analysis for a number of elements (say 6) should lead to improvements in versatility and reduce the time necessary to perform multielement analyses. The modifications required to provide AF as an option, on existing commercial AA and AE equipment, are rather simple to implement. Therefore, it seems that if or when sufficient demand for this technique appears, that instrumentation manufacturers can easily respond to the need.

2. Applications

Atomic absorption spectrophotometry is widely used to measure metals and other elements in trace amounts but not its chemical form. For example, AA can be used to specify the percentage of mercury in a liquid sample, but the concentration of methylmercury in fish is determined indirectly by knowing the percentage that is in a methyl form.

Once an element has been identified and one is required to quantify its existance in many different samples, then an AA system with an automated sample changer is suited to the task. The sequential analysis of many similar samples is readily performed. The simultaneous determination of two or more elements requires either two AA instruments or a dual channel AA. However, if a lamp turret option is used, different elements (presently about 6) can be sequentially examined by rotating the lamps.

3. Instrument Comparisons

It is a difficult task to compare a large number of complex instruments, particularly when a wide variety of options are offered.

The reader must consider cost, service, delivery, and reputation as crucial to any decision of which instrument to purchase. It is one intention of this section on atomic spectrometry to provide a uniform basis for technical comparisons (e.g., an attempt has been made to convert the data presented by the manufacturers to a common set of units).

A table could be drawn by the reader listing the instrument manufacturers and model numbers as column headings and a wide variety of individual considerations as row headings. Particular items of interest, e.g., detection limits, cost of hollow cathode lamps, guaranteed lamp life, time required to obtain replacement parts, compatibility with other laboratory equipment and procedures, data handling options, cost per sample, etc., are some candidates for row headings.

Occasionally a comparison of techniques will appear in the literature. One such comparison is given in Reference 11: "Hyland's normal and abnormal lyophilized serum and urine, as well as serum pools in the abnormal and normal ranges, were used as samples. Patient samples over a two-month period were split and run in duplicate on all three instruments to compare for significant differences from the means. The Hyland Control sera and urine were assayed daily on all the instruments to study daily variation.....A viscosity effect might play some role in patients whose plasma albumin concentrations are significantly shifted from the normal value. A series of experiments were done with artificial samples prepared by adding known amounts of sodium-free albumin (Pentrex Corporation) to determine if any such effect appeared."

The following brief statements summarize considerations when comparing a variety of atomic spectrometry instruments:

a. Atomic Absorption Spectrophotometry

1. Minimum detectable sensitivity: ppb or ng/g. Atomic absorption is one of the most sensitive commerically available techniques for determining the concentration of metals in liquid or gases.

2. Range of sensitivity: ppb to per cent. Eight or nine orders of magnitude.

3. Interferences: The flame units commonly use acetylene (C_2H_2) as the fuel, and compressed air (N_2, O_2, etc). as the oxidant, hence these elements may present an interferences. By changing

the fuel and the oxidant, specific interferences can be avoided.

4. Multi-parameter Capability: A large number of elements (~70) can be identified using this technique as well as some molecular determinations (SO_4, PO_4) indirectly. However, each element requires a special lamp (or a dual element lamp) and at present the maximum turret capacity is six lamps.

5. Sampling: For flame methods, the sample must be in solution or in suspension. Chemical separation is rarely needed. Usually a 1 ml liquid sample is used. For furnace methods, powders and solids are allowed as samples. For biomedical samples a nickel crucible is used.

6. Precision: About ±0.2% of the gross amount of the sample can be determined on a repeatable basis.

7. Accuracy: Depends on drift in single beam systems, or on frequency of calibration runs. In double beam systems, automatic recalibration is continuously performed

8. Calibration: Calibration samples containing a known concentration of the element of interest in a standard solution are usually satisfactory to ±1%.

9. Training: Moderate skill is required. Most manufacturers sponsor courses and provide literature which describes the operation of their equipment. One should obtain diagnostic, repair, and maintenance information with an instrument.

10. Requirements: Electrical power, bench space, fuel supply, exhaust vent, safety equipment.

11. Features: Optional equipment may include automated sample changing apparatus, printers, and recorders.

12. Cost: From about $3,000 to $12,000.

b. Atomic Emission Spectrophotometry

1. Minimum detectable sensitivity: ppb or ng/g. Atomic emission ranks with atomic absorption as one of the most sensitive commercially available techniques for determining the concentration of metallic elements in liquid samples.

2. Range of Sensitivity: ppb to per cent. Eight or nine orders of magnitude, estremely wide range.

3. Interferences: The plasma units may present an interference in the form of instabilities. However, AE is relatively free from interferences, even re-absorption of emitted photons is not considered a fundamental barrier to use of this technique.

4. Multiparameter Capability: AE is best suited to a broad qualitative search for unknown trace elements. The simultaneous analysis ability is one of the primary features of this technique.

5. Sampling: The sample may be in the gas liquid, or solid phase, and sample preparation is normally minimal.

6. Precision: About ±1% of the gross amount of the sample can be determined on a repeatable basis depending on the concentration of the metal.

7. Accuracy: A reasonably specific technique capable of resolving several closely spaced elements in the emission spectrum.

8. Calibration: Calibration samples containing a known concentration of the elements of interest are usually satisfactory to ±1%

9. Training: Moderate skill is required. Most manufacturers sponsor courses and provide literature which describes the operation of their equipment. One should obtain diagnostic, repair, and maintenance information with an instrument.

10. Requirements: Electrical power, bench space, safety equipment, fuel supply.

11. Features: Optional equipment may include automated sample changing apparatus, printers, and reorders.

12. Cost: From about $5000 to $12,000, depending on the basic analyzer and options.

4. Summary and Recommendations

Atomic absorption instruments have benefited from the sizable amount of research and development effort that has been invested to refine this technique. AA is the most widely accepted of the atomic spectrometry techniques considered here and as such is the standard by which the others are judged. The furnace approach has merit for atomizing a sample and provides a longer residence time in the light beam. AA is currently the best technique for analyzing a large number of samples to determine the concentration of a known element.

Atomic emission is useful for determining which elements are present in a sample. In general, the minimum detectable concentration limits are comparable to AA and many manufacturers offer AE as an option on AA instruments. The capability for simultaneous multi-parameter analysis is very useful for some biomedical survey work.

Atomic fluorescence does not have a clear superiority for any particular element, however the prospects of performing simultaneous quantitative analysis for a number of elements. is a needed feature. As more multielement analyses are required, the time necessary to obtain a result will be of increasing importance.

No government funding to improve this technique is needed since an adequate pace of research and development is being supported by corporations in the private sector. However, a critical evaluation should be performed to compare AA, AE, and AF with other techniques.

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15. Jarrell-Ash, manufacturer's specifications. See instrument notes.

16. Pye-Unicam, manufacturer's specifications. See instrument notes.

17. SpectraMetrics, manufacturer's specifications. See instrument notes.

TABLE OF

ATOMIC SPECTROMETRY INSTRUMENTATION

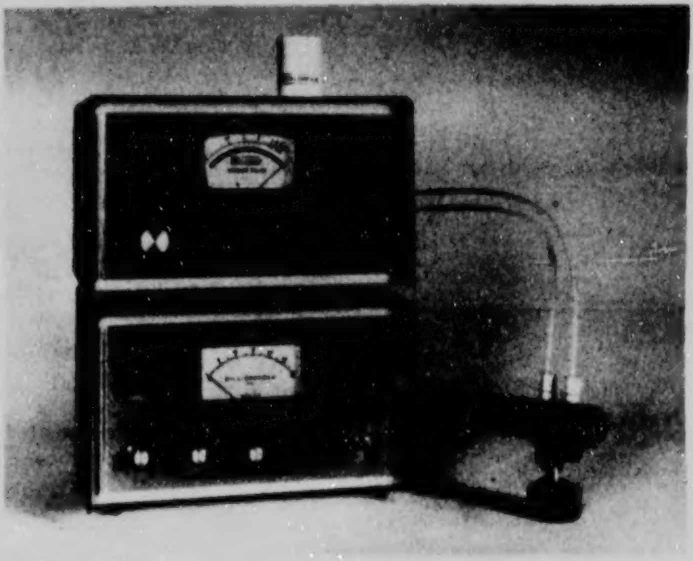
Instrument	Beam	Lamps	Flame Emission	Atomic Fluorescence	Cost	Remarks
Fisher, J-A						
810	Double	2			$15,300.	Two channel, dual monochromator
GCA/McPherson						
EU-703 D	Single	4		Yes	$ 6,500.	
Instrumentation Labs						
151	Single	1,2, or 4	Yes	No	$ 6,500.	Background Correction Optional
251	Double/ Single	1,2, or 4	"	"	$ 7,900.	Background Correction Optional
351	Double	6	"	"	$ 9,400.	Same as above
453	Double	6	Yes	No	$14,000.	
455	—				$ 4,350.	Flameless
Perkin-Elmer						
103	Single	1	Yes	No	$ 4,900.	Analog readout
107	"	1	"	"	$ 5,500.	Digital readout
305 B	Double	1	"	"	$ 8,950.	Analog readout
305 BG	"	1	"	"	$ 8,950.	" "
306	"	1	"	"	$ 9,990.	Digital readout
360	"	1	"	"	$ 6,750.	
503	"	1	"	"	$15,000.	
HGA-2100	—	—	—	—	$ 4,290.	Furnace
Pye Unicam						
SP 1900	Double	6	Yes	No	$11,950.	
SP 1950	"	1	"	"	$ 9,950.	

Instrument	Beam	Lamps	Flame Emission	Atomic Fluorescence	Cost	Remarks
Varian 1000	Single	4	Yes	No	$ 4,790.	
1100	"	4	"	"	$ 5,990.	
1200	"	4	"	"	$ 6,550.	
AA-6	"	4	"	"	$11,000.	Integration mode
63	—	—	—	—	$ 4,300.	Flameless

130

Hollow Cathode Lamps

Barnes, Glomax Hollow Lamps



Class	Laboratory
Principle of Operation	Demountable hollow cathode lamps, power supply, gas control unit
Multiparameter Capability	60 elements
Performance	Regulation: Less than 0.1% change in lamp current for a 10% change in line voltage. Stability: Less than 0.05% drift in lamp current over a one-hour period after 30 min warm-up.
Operation	Ignition Voltage: 300 Vdc min Operating Voltage: 140 to 25- Vdc Operating Current: 100 mg max DC Calibration: Maintenance
Requirements	Power: 110-220 Vac, 50-60 Hz Weight: Power supply - 9.07 kg (20 lb) Gas control - 6.35 kg (14 lb) Dimensions: Power supply - 33.7 cm W, 20.3 cm H, 22.9 cm D (13.3" x 8" x 9") Gas control - 33.7 cm W, 20.3 cm H, 22.9 cm D (13.3" x 8" x 9") Lamps - 3.8 cm dia, 12.7 cm long (1.5" D, 5" L)
Features	Vacuum Pump: 0.05 Torr, capacity of 20 l/min at ATM Ionizing Gas: Tank and regulator for pure, dry Helium, Neon, or Argon Options: Lamp mounts for AA Spectrometers
References	Manufacturer's Specifications

Cost	Glomax lamp, fittings, 10 cathodes	$395
	GPS-1 Power supply	$795
	GCU-1 Gas Control Unit	$550
	GHE-1 Heat Exchanger	$ 25
	Lamp Cathodes: Ca	$ 14
	Cr	$ 15
	Cu	$ 10
	Fe	$ 14
	Pb	$ 18
	Mg	$ 13
	Mn	$ 15
	Hg	$ 14
	Na	$ 14
	Ti	$ 15

Address

Barnes Engineering Company
30 Commerce Road
Stamford, Ct 06902
ATTN: Katny Pellman
(203) 348-5381

H2O-MET
Atomic Spectrometry
F & J
Sept. 1975

Atomic Absorption

F and J Scientific Hg/As/Se Kit

Class	Laboratory
Category	Air: Ambient, Source, or Vehicular Water: Fresh, Waste, or Saline Biomedical: Tissue, Urine, or Blood
Principle of Operation	Accessories for Atomic Absorption Spectrophotometers: Kit for determining Mercury, Arsenic, or Selenium, Glassware, solutions, syringes, etc.
Lower Detectable Limit	As 1.0 ppb Hg 0.2 ppb Se 1.0 ppb
Range	
Interferences	
Multiparameter Capability	
Sampling	Method: Batch, samples/min Volume: Capacity: One sample at a time
Performance	Electronics: Hollow cathode tubes

MULTI-ELEMENT HOLLOW CATHODE LAMPS

Part No.	Price	Part No.	Price
HC-Al/Ca	$130.00	HC-Co/Ni	$150.00
HC-Al/Ca/Mg	145.00	HC-Cu/Au/Ni	210.00
HC-Al/Ca/Fe/Mg	195.00	HC-Co/Cu/Mo/Zn	200.00
HC-Al/Ca/Li/Mg	165.00	HC-Cu/Fe	150.00
HC-As/Ni	170.00	HC-Cu/Mn	120.00
HC-As/Sb/Bi	210.00	HC-Cu/Ni	150.00
HC-As/Se/Te	210.00	HC-Cu/Fe/Mn	170.00
HC-Ba/Ca/Sr	165.00	HC-Cu/Fe/Mo	180.00
HC-Ba/Ca/Sr/Mg	200.00	HC-Cu/Mo/Zn	170.00
HC-Cd/Cu/Pb/Zn	200.00	HC-Cu/Au/Fe/Ni	210.00
HC-Cd/Pb/Ag/Zn	200.00	HC-Cu/Fe/Mn/Zn	195.00
HC-Ca/Zn	125.00	HC-Cu/Pb/Ag/Zn	195.00
HC-Ca/Ba/Sr	165.00	HC-Cu/Pb/Sn/Zn	195.00
HC-Ca/Mg/Sr	170.00	HC-Cu/Fe/Pb/Ni/Zn	230.00
HC-Ca/Mg/Zn	170.00	HC-Ga/Cu	170.00
HC-Cr/Cu	150.00	HC-Au/Ni	160.00
HC-Cr/Mn	150.00	HC-Au/Ag	155.00
HC-Cr/Co/Ni	180.00	HC-In/Ag	170.00
HC-Cr/Fe/Mn/Ni	195.00	HC-Pb/Ag/Zn	205.00
HC-Cr/Co/Cu/Mn/Ni	210.00	HC-Pb/Cd/Ag/Zn	200.00
HC-Cr/Co/Cu/Fe/Mn/Ni	230.00	HC-Mg/Zn	150.00
HC-Co/Cu	150.00	HC-Ni/Se	160.00
HC-Co/Fe	150.00	HC-K/Na	150.00

Performance (Contd)

SINGLE ELEMENT HOLLOW CATHODE LAMPS

Part No.	Element	Price	Part No.	Element	Price
HC-Al	Aluminum	$ 95.00	HC-Nd	Neodymium	$150.00
HC-Sb	Antimony	115.00	HC-Ni	Nickel	95.00
HC-As	Arsenic	145.00	HC-Nb	Niobium	125.00
HC-Ba	Barium	120.00	HC-Os	Osmium	215.00
HC-Be	Beryllium	150.00	HC-Pd	Palladium	135.00
HC-Bi	Bismuth	125.00	HC-Pt	Platinum	150.00
HC-B	Boron	120.00	HC-K	Potassium	135.00
HC-Cd	Cadmium	110.00	HC-Pr	Praseodymium	160.00
HC-Ca	Calcium	95.00	HC-Re	Rhenium	160.00
HC-Ce	Cerium	155.00	HC-Rh	Rhodium	170.00
HC-Cs	Cesium	135.00	HC-Rb	Rubidium	135.00
HC-Cr	Chromium	95.00	HC-Ru	Rutherium	160.00
HC-Co	Cobalt	95.00	HC-Sm	Samarium	155.00
HC-Cu	Copper	95.00	HC-Sc	Scandium	200.00
HC-Dy	Dysprosium	160.00	HC-Se	Selenium	125.00
HC-Er	Erbium	160.00	HC-Si	Silicon	125.00
HC-Eu	Europium	190.00	HC-Ag	Silver	100.00
HC-Gd	Gadolinium	160.00	HC-Na	Sodium	135.00
HC-Ga	Gallium	130.00	HC-Sr	Strontium	130.00
HC-Ge	Germanium	135.00	HC-Ta	Tantalum	125.00
HC-Au	Gold	140.00	HC-Te	Tellurium	130.00
HC-Hf	Hafnium	165.00	HC-Tb	Terbium	150.00
HC-Ho	Holmium	160.00	HC-Tl	Thallium	115.00
HC-In	Indium	130.00	HC-Th	Thorium	150.00
HC-Ir	Iridium	170.00	HC-Tm	Thulium	180.00
HC-Fe	Iron	95.00	HC-Sn	Tin	125.00
HC-La	Lanthanum	160.00	HC-Ti	Titanium	105.00
HC-Pb	Lead	115.00	HC-W	Tungsten	105.00
HC-Li	Lithium	120.00	HC-U	Uranium	195.00
HC-Lu	Lutetium	190.00	HC-V	Vanadium	145.00
HC-Mg	Magnesium	95.00	HC-Yb	Ytterbium	155.00
HC-Mn	Manganese	100.00	HC-Y	Yttrium	150.00
HC-Hg	Mercury	115.00	HC-Zn	Zinc	95.00
HC-Mo	Molybdenum	95.00	HC-Zr	Zirconium	125.00

Gas Control: Regulators, burners, flame heads, nebulizers, and spare parts

Operation
Calibration: 62 standard solutions available (1,000 ppm)
Procedure: Described in booklet
Maintenance:
Training Required: Minimal

Requirements
Power:
Weight:
Dimensions:

Features:

References: Manufacturer's Specifications

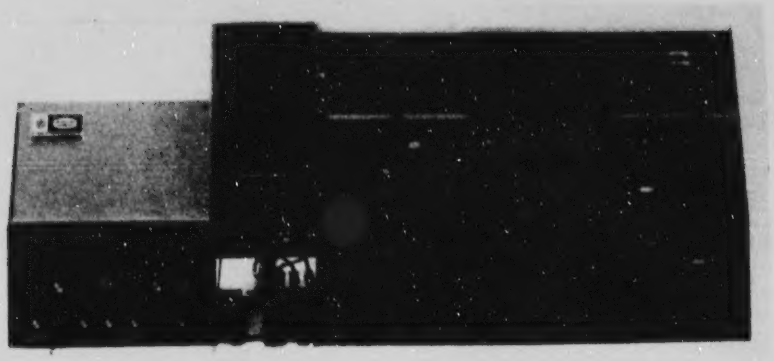
Cost

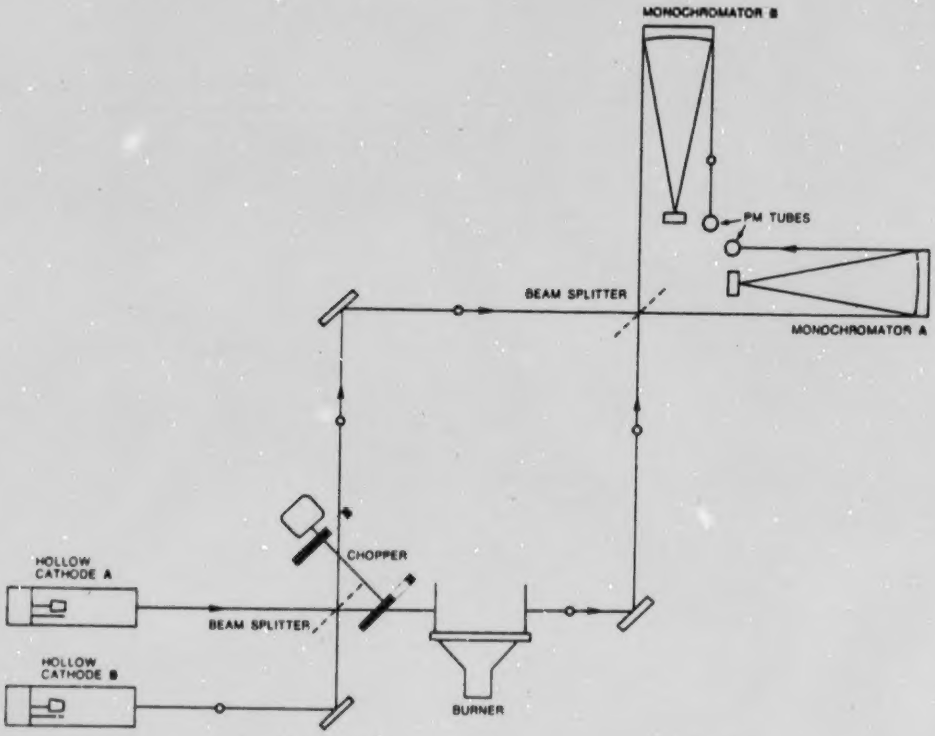
Hg/As/Se Kit	$250
Hg Kit	$200
As/Se Kit	$150

Address
F & J Scientific
79 Far Horizon Dr
Monroe, CT 06468
(203) 268-3335

Atomic Absorption Spectrophotometer

Fisher, Jarrell-Ash, Model 810




MONOCHROMATOR B
PM TUBES
BEAM SPLITTER
MONOCHROMATOR A
CHOPPER
HOLLOW CATHODE A
BEAM SPLITTER
HOLLOW CATHODE B
BURNER

Class	Laboratory
Category	Air: Ambient, Source, or Vehicular Water: Fresh, Waste, or Saline Biomedical: Tissue, Urine, or Blood
Principle of Operation	Atomic Absorption Spectrophotometer: Double beam, two channel, premix burner chamber, electric flame ignition, auto-zero circuit, signal integration mode, digital readout of concentration.

Lower Detectable Limit

Detection Limits

*Aluminum	0.05 μg/ml	Copper	0.003 μg/ml	Rhodium	0.015 μg/ml
Antimony	0.1	Gold	0.02	Rubidium	0.005
†Arsenic	0.2	Iron	0.01	†Selenium	0.1
Barium	0.02	Lead	0.03	*Silicon	0.2
*Beryllium	0.002	Lithium	0.002	Silver	0.003
Bismuth	0.05	Magnesium	0.0004	Sodium	0.001
Cadmium	0.003	Manganese	0.003	Strontium	0.01
Calcium	0.005	*Molybdenum	0.03	‡Tin	0.05
‡Cesium	0.02	Nickel	0.01	*Titanium	0.1
Chromium	0.005	Platinum	0.2	*Vanadium	0.03
Cobalt	0.01	Potassium	0.003	Zinc	0.003

**Acetylene/nitrous oxide flame*
†Argon – supported hydrogen flame
‡Hydrogen/air flame
Others determined with acetylene/air.

Range

ppb to %

Interferences

Minimal for most analysis. Interferences can be overcome by carefully selecting the proper flame conditions, and/or by adding chemical interference suppresants to the sample.

Multiparameter Capability

70 elements

Sampling

Method: Batch
Volume:
Capacity: One sample at a time
Modes:
1. Two metals simultaneously in the same sample.
2. Both channels can be used for atomic absorption, or one for AA and the other for flame emission.
3. A minus B mode allows one channel to measure and automatically subtract background absorption from the other.
4. In the A/B ratio mode, one channel can be used to monitor an internal standard, while the other one makes the analytical measurement.

Performance

Electronics: Synchronous ratio detection with log-to-linear conversion, signal integration, and digital readout. Solid-state plug-in circuit cards.

Linearity:
Stability:
Scale Expansion: 20x
Detector: Photomultiplier
Zero Drift:
Background:

Monochromator: Ebert, 0.4 meter focal length

Grating: Quartz 58 x 58 mm, 1180 grooves/mm, blazed at 300 nm
Range: 190 to 900 nm
Accuracy: ±0.2 nm
Dispersion: 20.8 A/mm
Spectral Slit-width: 0.3, 2, 5, 10, 20 Å, switch selectable

Gas Control: Four separate fuel and oxidant flow meters, rotary control valves, push button ignition, safety interlock system.

Burner: Pre-mix laminar-flow with 5 and 10 cm slots. Corrosion resistant construction.

Adjustments: Vertical, horizontal, and rotational with indicating scales.

Operation

Calibration: via standards
Procedure:
Maintenance: Moderate
Training Required: Moderate, courses available

Requirements

Power: 115 Vac, 60 Hz or 230 Vac, 50 Hz, 300 watts
Weight: 215 kg (475 lbs)
Dimensions: 56 cm, 130 cm, 69 cm (22 in. D, 51 in. L, 27 in. H)

Features

Options: Automatic Gas Control Programmer
Strip-chart Recorder
Trace Metal Accessory

References

Manufacturer's Specifications

Cost

Model 810 $15,300
Lamps

Single-Element Lamps

Element	Analytical Line	Fisher Catalog No.
Aluminum	309.2 mμ	JA 45-452
Antimony	217.6 mμ	JA 45-461
Arsenic	193.7 mμ	JA 45-315
Barium	553.6 mμ	JA 45-480
††Beryllium	234.9 mμ	JA 45-567
Bismuth	223.1 mμ	JA 45-469
Boron	249.7 mμ	JA 45-568
Cadmium	228.8 mμ	JA 45-462
Calcium	422.7 mμ	JA 45-440
*Cerium	520.0 mμ	JA 45-569
*Cesium	852.1 mμ	JA 45-441
Chromium	357.9 mμ	JA 45-454
Cobalt	240.7 mμ	JA 45-456
Copper	324.7 mμ	JA 45-458
*†Copper	249.2 mμ	JA 45-490
Dysprosium	421.2 mμ	JA 45-586
Erbium	400.8 mμ	JA 45-571
Europium	459.4 mμ	JA 45-572
Gadolinium	368.4 mμ	JA 45-573
Gallium	287.4 mμ	JA 45-470
Germanium	266.2 mμ	JA 45-313
Gold	242.8 mμ	JA 45-467
Hafnium	307.2 mμ	JA 45-303
Holmium	410.4 mμ	JA 45-578
Hydrogen	Continuum	JA 45-316
Indium	304.0 mμ	JA 45-471
Iridium	285.0 mμ	JA 45-577
Iron	248.3 mμ	JA 45-455
Lanthanum	392.8 mμ	JA 45-495
Lead	283.3 mμ	JA 45-468
Lithium (Natural)	670.8 mμ	JA 45-444
*Lithium-6	670.8 mμ	JA 45-579
*Lithium-7	670.8 mμ	JA 45-580
*Lutetium	328.2 mμ	JA 45-581
Magnesium	285.2 mμ	JA 45-451
Manganese	279.5 mμ	JA 45-472
Mercury	253.7 mμ	JA 45-493
Molybdenum	313.3 mμ	JA 45-460
Neodymium	463.4 mμ	JA 45-582
Nickel	232.0 mμ	JA 45-457
Niobium	334.9 mμ	JA 45-488
Osmium	290.9 mμ	JA 45-584
Palladium	247.6 mμ	JA 45-475
Platinum	265.9 mμ	JA 45-466
Potassium	766.5 mμ	JA 45-484
Praseodymium	495.1 mμ	JA 45-585
Rhenium	346.0 mμ	JA 45-489
Rhodium	343.5 mμ	JA 45-476
Rubidium	780.0 mμ	JA 45-443
Ruthenium	349.9 mμ	JA 45-586
Samarium	429.7 mμ	JA 45-587
Scandium	391.2 mμ	JA 45-309
Selenium	196.0 mμ	JA 45-477
Silicon	251.6 mμ	JA 45-479
Silver	328.1 mμ	JA 45-483
Sodium	589.0 mμ	JA 45-485
Strontium	460.7 mμ	JA 45-481
Tantalum	271.4 mμ	JA 45-488
*Tellurium	214.3 mμ	JA 45-473
*Terbium	432.6 mμ	JA 45-589
††Thallium	276.8 mμ	JA 45-570
*Thorium	324.5 mμ	JA 45-590
*Thulium	410.5 mμ	JA 45-591
Tin	286.3 mμ	JA 45-463
Titanium	364.3 mμ	JA 45-592
Tungsten	400.9 mμ	JA 45-465
*Uranium	351.5 mμ	JA 45-447
Vanadium	318.4 mμ	JA 45-453
Ytterbium	398.8 mμ	JA 45-593
Yttrium	410.2 mμ	JA 45-594
Zinc	213.9 mμ	JA 45-459
Zirconium	360.1 mμ	JA 45-482

*Not High Spectral Output type.
†With quartz window which permits use of secondary UV lines of copper.
††Not manufactured by Westinghouse.

Multi-Element Lamps

Elements	Fisher Catalog No.
Arsenic - Nickel	JA 45-434
Arsenic - Selenium - Tellurium	JA 45-598
Barium - Calcium - Strontium - Magnesium	JA 45-478
Barium - Calcium - Strontium	JA 45-437
Calcium - Aluminum - Magnesium	JA 45-450
Calcium - Iron - Aluminum - Magnesium	JA 45-310
Calcium - Magnesium - Aluminum - Lithium	JA 45-436
Calcium - Magnesium - Zinc	JA 45-311
Calcium - Zinc	JA 45-304
Chromium - Copper	JA 45-306
Chromium - Nickel - Iron - Manganese	JA 45-442
Cobalt - Chromium - Copper - Iron - Nickel - Manganese	JA 45-599
Copper - Cobalt	JA 45-305
Copper - Gallium	JA 45-431
**Copper - Iron	JA 45-312
Copper - Lead - Zinc - Silver	JA 45-448
Copper - Manganese	JA 45-491
**Copper - Zinc - Iron - Manganese	JA 45-492
Copper - Zinc - Lead - Cadmium	JA 45-597
Copper - Zinc - Lead - Tin	JA 45-438
Copper - Zinc - Molybdenum	JA 45-496
Copper - Zinc - Molybdenum - Cobalt	JA 45-596
Gold - Copper - Iron - Nickel	JA 45-307
Gold - Nickel	JA 45-433
Iron - Copper - Manganese	JA 45-435
Iron - Copper - Nickel - Lead - Zinc	JA 45-302
*Magnesium - Zinc	JA 45-314
Molybdenum - Copper - Iron	JA 45-301
Selenium - Nickel	JA 45-497
Sodium - Potassium	JA 45-439
Zinc - Silver - Lead - Cadmium	JA 45-308

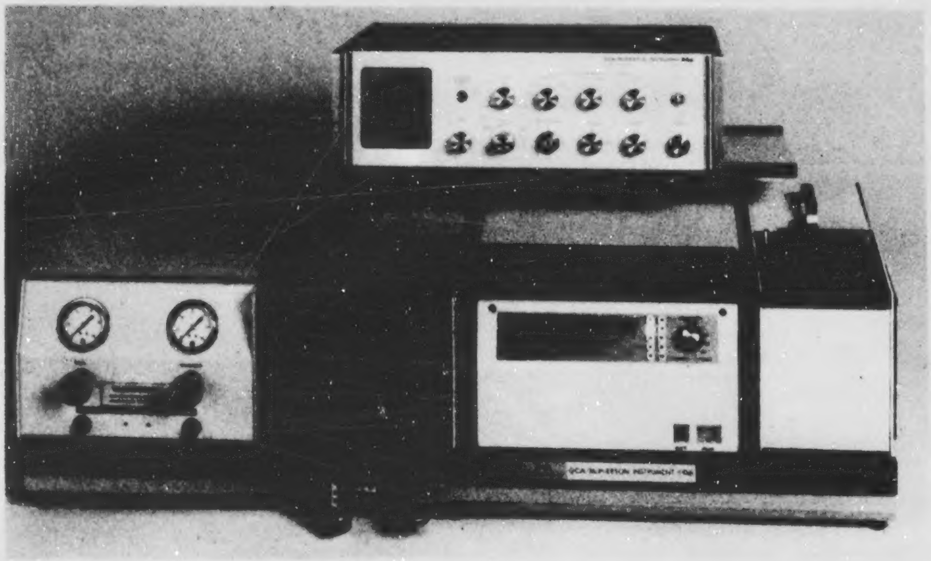
High Spectral Output tubes.

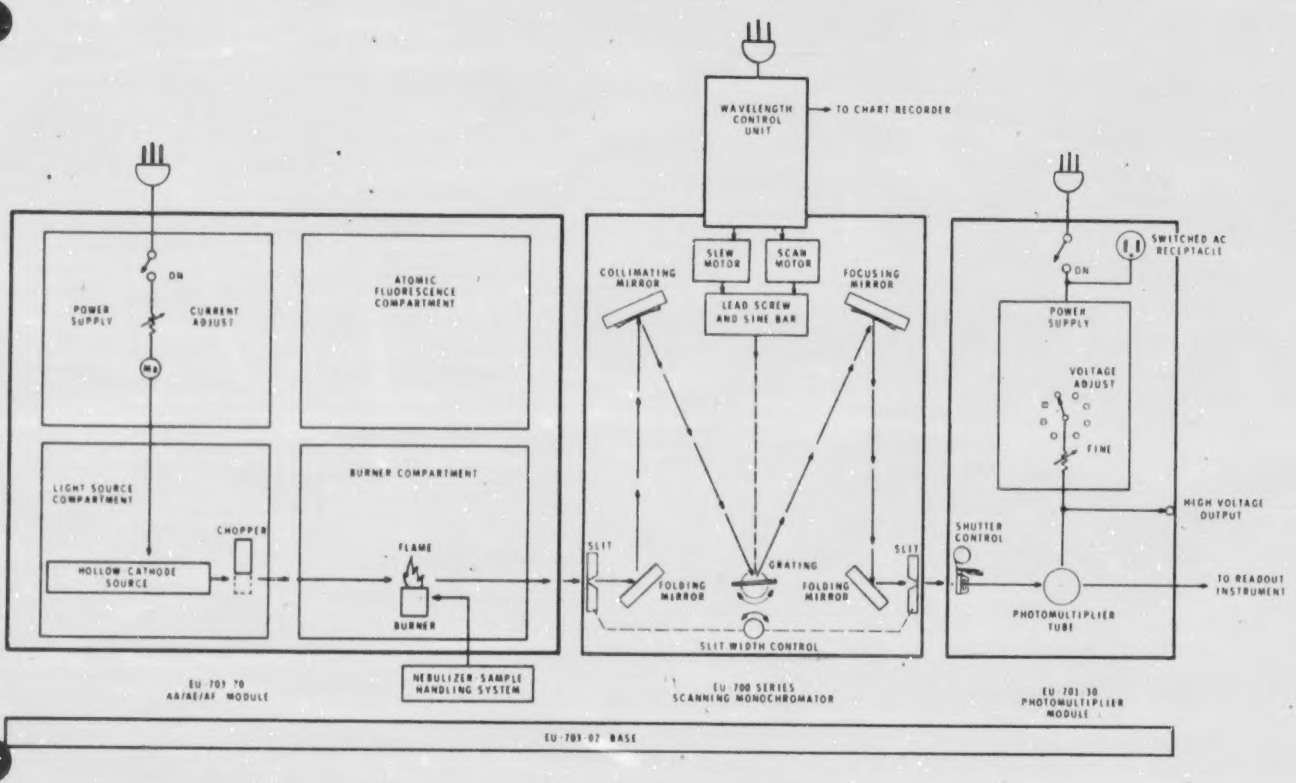
Address

Fisher, Jarrell-Ash
711 Forbes Avenue
Pittsburgh, PA 15219
ATTN: Mr. Zanto
(412) 562-8300

Atomic Absorption, Spectrophotometer

GCA/McPherson, Model EU-703D




WAVELENGTH CONTROL UNIT
TO CHART RECORDER
ON
POWER SUPPLY
CURRENT ADJUST
ATOMIC FLUORESCENCE COMPARTMENT
LIGHT SOURCE COMPARTMENT
BURNER COMPARTMENT
CHOPPER
FLAME
HOLLOW CATHODE SOURCE
BURNER
NEBULIZER-SAMPLE HANDLING SYSTEM
EU-703-70 AA/AE/AF MODULE
SLEW MOTOR
SCAN MOTOR
COLLIMATING MIRROR
FOCUSING MIRROR
LEAD SCREW AND SINE BAR
SLIT
GRATING
SLIT
FOLDING MIRROR
FOLDING MIRROR
SLIT WIDTH CONTROL
EU-700 SERIES SCANNING MONOCHROMATOR
SWITCHED AC RECEPTACLE
ON
POWER SUPPLY
VOLTAGE ADJUST
FINE
HIGH VOLTAGE OUTPUT
SHUTTER CONTROL
PHOTOMULTIPLIER TUBE
TO READOUT INSTRUMENT
EU-701-30 PHOTOMULTIPLIER MODULE
EU-703-02 BASE

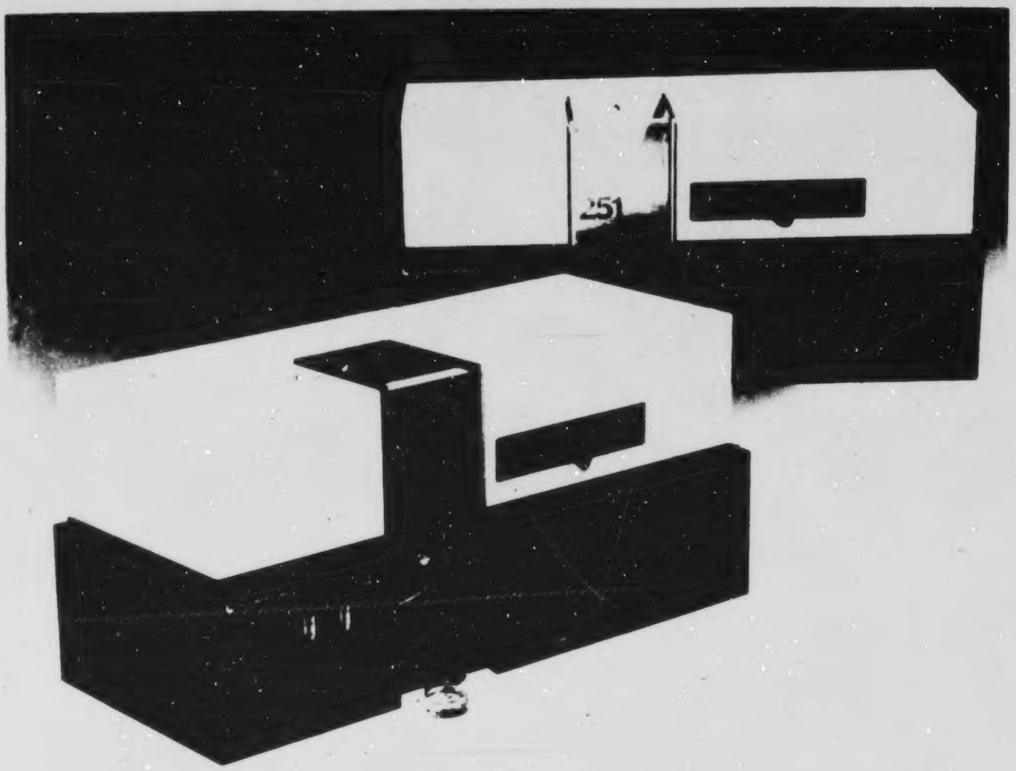
Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Atomic absorption, emission and fluorescence spectrophotometer, single beam, flame positioning, four lamp turret
Lower Detectable Limit	
Range	
Interferences	
Multiparameter Capability	
Sampling	Method: Batch Volume: Capacity:
Performance	Electronics: Linearity: Stability: Scale Expansion: 0-0.1 A, 0-0.5 A, 0-1.0 A, 0-2.0 A, -0.3-+9.7 A; 0-10, 0-50, 0-100% T Detector: IP28A Photomultiplier Zero Drift: ±0.001 A/hr Span Drift: Monochromator: Czerny-Turner, 350 mm Grating: 1180 g/mm; blazed at 250 nm, 48 x 48 mm Wavelength Range: 185 to 750 nm 185 to 1000 nm, optional Wavelength Tracking Accuracy: ±0.1 nm Wavelength Reproducibility: ±0.01 nm Resolution: 0.1 nm Dispersion: 2 nm/mm Slit Width: Manual, continuously adjustable between 5 and 2000 microns Gas Control: Toggle valves Fuel: Air, O_2 Oxidant: C_2H_2, H_2 Flow Indicator: Dial gauges Venting:
Operation	Calibration: Standard samples Procedure: Manual provided Training: Requires about hours Unattended Period: Maintenance: Factory service
Requirements	Power: 105-125 Vac, 50/60 Hz, 135 Watts Weight: 67 kg (148 lb) Dimensions: 98 cm W, 57 cm D, 38 cm H, 71 cm H with chimney (38.5" W, 22.5" D, 15" H, 28" H with chimney)

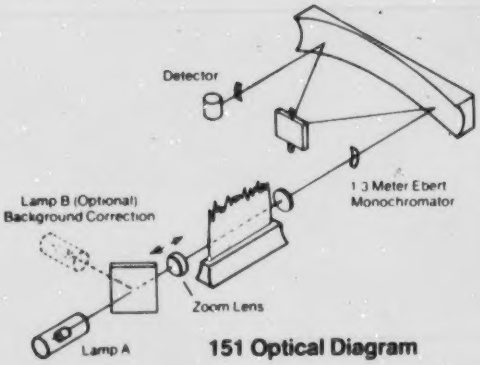
Features	Burner positioning for X-Y or Y-Z axes adjustment Output: Recorder, digital display of photometric and wavelength data; direct reading of A, %T, I, Difference, Concentration, and dA/dt (Rate)
References	Manufacturer's Bulletin
Cost	Model EU-703D $6,500
Address	GCA/McPherson Instrument 530 Main Street Acton, MA 01720 (617) 263-7733

H2O-MET
Atomic Spectrometry
Instrumentation Lab 1
Sept. 1975

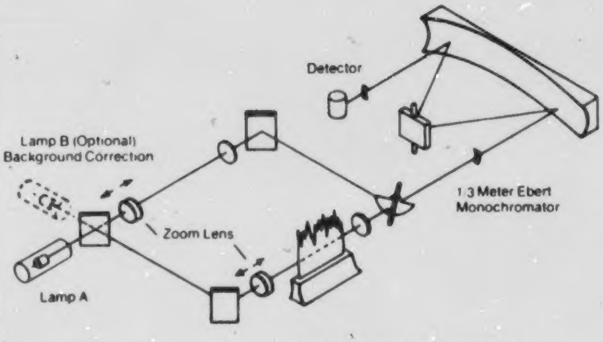
Atomic Absorption/Emission Spectrophotometers

Instrumentation Laboratory, Models 151, 251




Detector
Lamp B (Optional)
Background Correction
1.3 Meter Ebert
Monochromator
Zoom Lens
Lamp A

151 Optical Diagram


Detector
Lamp B (Optional)
Background Correction
1.3 Meter Ebert
Monochromator
Zoom Lens
Lamp A

251 Optical Diagram

Class

Laboratory

Categories

Air: Source, Vehicular, Ambient
Water: Fresh, Saline, Waste
Biomedical: Blood, Tissue, Serum, Urine

Principle of

Model 151: Single beam, manual zoom lens; modes: absorbance (A), flame emission (FE), absorbance (A-B) option

Model 251: Double beam or single beam dual automatic zoom lens: absorbance (A), absorbance (B), flame emission (FE), and absorbance (A-B) Optional

Lower Detectable Limit

Sensitivity is defined as the concentration of an element in an aqueous solution which gives rise to 1% absorption (0.0044 Absorbance).

Detection Limit is defined as that concentration of an element which provides a signal equal to twice the standard deviation of a series of ten blank corrected readings of the element at a concentration close to the blank level.

Element	Sensitivity (μg/ml)	Detection Limit (μg/ml)
Ag Silver	0.04	0.003
Al Aluminum	0.43	0.04
As Arsenic	0.63	0.21 0.001*
Au Gold	0.1	0.014
B Boron	8.0	2.0
Ba Barium	0.17	0.015
Be Beryllium	0.014	0.0026
Bi Bismuth	0.22	0.07
Ca Calcium	0.02	0.001
Cd Cadmium	0.01	0.002
Co Cobalt	0.05	0.005
Cr Chromium	0.04	0.003
Cs Cesium	0.058	0.019
Cu Copper	0.04	0.004
Er Erbium	0.47	0.07
Fe Iron	0.05	0.003
Hg Mercury		0.0005*
K Potassium	0.02	0.003
Li Lithium	0.023	0.0016
Mg Magnesium	0.004	0.0002
Mn Manganese	0.03	0.003
Mo Molybdenum	0.28	0.046
Na Sodium	0.005	0.00023
Ni Nickel	0.05	0.007
Pb Lead	0.08	0.01
Pr Praseodymium	28.1	7.3
Pt Platinum	1.0	0.098
Rb Rubidium	0.02	0.0034
Re Rhenium	8.5	0.73
Rh Rhodium	0.12	0.022
Sb Antimony	0.28	0.06 0.006*
Sc Scandium	0.25	0.03
Se Selenium	0.11	0.16 0.001*
Si Silicon	1.3	0.35
Sn Tin	0.88	0.16
Sr Strontium	0.06	0.001
Ta Tantalum	12.0	0.94
Te Tellurium	0.21	0.07
Ti Titanium	1.5	0.12
Tl Thallium	0.23	0.03
V Vanadium	0.96	0.05
W Tungsten	16.9	1.4
Y Yttrium	1.69	0.3
Yb Ytterbium	0.077	0.005
Zn Zinc	0.007	0.0026

Note: All sensitivities and detection limits were obtained using an air-acetylene or nitrous oxide-acetylene flame unless otherwise noted. Potassium was added to the aqueous standards to suppress ionization for easily ionized elements.

*Hydride Generator

Range

Absorbance Range: ±3.000
Concentration: Up to 7000

Interferences

Multiparameter Capability

See table; one element at a time

Sampling

Method: Batch or automatic, sample in solution
Volume: 1 μl to 3 ml dependent upon atomization source
Capacity: Up to 12 determinations per minute

Performance

Electronics: Solid state, LED readout, 4.5 digits

Linearity: Varies with element determined
Stability: 0.005% short term
Scale Expansion: 0.3x to 50x
Detector: R372 photomultiplier
Readout: Four digit illuminated display
Response Time: Integral mode at 1/16, 1/4, 1, 4, or 16 sec
Other: AutoZero, Offline calibration, Four lamp turret with warmup

Monochromator: Ebert mount, 0.33 m

Grating: 1200/mm blazed at 250 nm
32 x 32 mm
Wavelength Range: 190 to 900 nm
Wavelength Accuracy: Better than 0.05 nm
Wavelength Reproducibility: Better than 0.1 nm
Resolution: 0.04 nm, first order
Reciprocal Dispersion: 2.5 nm/mm
Slit Width: Curved variable in 7 steps from 10 to 640 μm

Gas Control: Solenoid valving, constant level burner drain system, electric ignition, pressure orifice flow control

Oxidant: Air or N_2O
Fuel: C_2H_2
Venting: 10.2 cm dia., 28 l/min (4" dia., 100 cf/min)

Operation

Calibration: Standard samples
Procedure: Manual provided
Training: Requires about 20 hours depending upon number and complexity of analyses
Unattended Period: None
Maintenance: 12 service centers in U.S.

Requirements

Power: 100, 115, or 230 Vac ± 20%, 50 or 60 Hz, 230 W
Weight: Model IL 151 -- 127 kg (280 lb)
Model IL 251 -- 134 kg (295 lb)
Dimensions: 50.8 cm H, 109.1 cm L, 45.7 cm D (20" H, 43" L, 18" D)

Features

Output: Digital meter; recorder, four detection modes; automatic update, manual update, peak height and peak area, built-in test circuit, automatic zero, curve correction

Options:

Electric wavelength scan	$400
Automatic gas safety system	$900
Background correction & Deuterium lamp	$1,150
4-lamp turret	$800
Dual grating monochromator	$500

References

Manufacturer's Bulletin

Cost

Model IL 151	$6,500
Model IL 251	$7,900
Model IL 351	$9,400

H2O-MET
Atomic Spectrometry
Instrumentation Lab 1
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HOLLOW CATHODE LAMPS, Single Element

Cat. No.	Price	Cathode Element	Win/Gas*
62809	$115.00	Aluminum - Al	P/N
62931	140.00	Antimony - Sb	Q/N
62836	170.00	Arsenic - As	Q/N
62834	145.00	Barium - Ba	P/N
63300	170.00	Beryllium - Be	Q/N
62932	135.00	Bismuth - Bi	Q/N
62916	140.00	Boron - B	Q/A
62933	140.00	Cadmium - Cd	Q/N
62610	120.00	Calcium - Ca	P/N
62977	170.00	Cerium - Ce	Q/N
62823	160.00	Cesium - Cs	P/N
62934	115.00	Chromium - Cr	Q/N
62928	115.00	Cobalt - Co	Q/N
63041	115.00	Copper - Cu	Q/N
62827	175.00	Dysprosium - Dy	Q/N
62828	175.00	Erbium - Er	Q/N
62845	230.00	Europium - Eu	Q/N
62965	175.00	Gadolinium - Gd	Q/N
62833	160.00	Gallium - Ga	Q/N
63472	170.00	Germanium - Ge	Q/N
62935	170.00	Gold - Au	Q/N
63180	180.00	Hafnium - Hf	Q/N
62829	175.00	Holmium - Ho	Q/N
62996	150.00	Indium - In	Q/N
63145	185.00	Iridium - Ir	Q/N
62810	115.00	Iron - Fe	Q/N
63049	180.00	Lanthanum - La	Q/N
62927	140.00	Lead - Pb	Q/N
63060	145.00	Lithium - Li	P/N
63009	205.00	Lutetium - Lu	Q/N
62968	115.00	Magnesium - Mg	Q/N
62936	120.00	Manganese - Mn	Q/N
62847	135.00	Mercury - Hg	Q/A
62937	115.00	Molybdenum - Mo	Q/N
62847	135.00	Mercury - Hg	

HOLLOW CATHODE LAMPS, Single Element

Cat. No.	Price	Cathode Element	Win/Gas*
62979	$180.00	Neodymium - Nd	Q/N
62819	115.00	Nickel - Ni	Q/N
62858	150.00	Niobium - Nb	Q/N
63144	255.00	Osmium - Os	Q/A
62969	155.00	Palladium - Pd	Q/N
63474	180.00	Platinum - Pt	Q/N
62863	160.00	Potassium - K	P/N
62981	175.00	Praseodymium - Pr	Q/N
62942	175.00	Rhenium - Re	Q/N
62997	.205.00	Rhodium - Rh	Q/N
62824	155.00	Rubidium - Rb	P/N
63138	180.00	Ruthenium - Ru	Q/A
62818	175.00	Samarium - Sm	Q/N
63181	230.00	Scandium - Sc	Q/N
62938	155.00	Selenium - Se	Q/N
62939	145.00	Silicon - Si	Q/N
62806	120.00	Silver - Ag	Q/A
63059	160.00	Sodium - Na	P/N
62835	155.00	Strontium - Sr	P/N
62859	150.00	Tantalum - Ta	Q/A
62940	155.00	Tellurium - Te	Q/N
62848	170.00	Terbium - Tb	Q/N
63301	155.00	Thallium - Tl	Q/N
63027	170.00	Thorium - Th	Q/N
63007	205.00	Thulium - Tm	Q/N
62941	150.00	Tin - Sn	Q/N
62991	125.00	Titanium - Ti	Q/N
62844	125.00	Tungsten - W	Q/N
62826	215.00	Uranium - U	Q/N
62973	175.00	Vanadium - V	Q/N
62983	185.00	Ytterbium - Yb	Q/A
62987	170.00	Yttrium - Y	Q/N
62811	120.00	Zinc - Zn	Q/N
62860	145.00	Zirconium - Zr	Q/A

HOLLOW CATHODE LAMPS, Multi-Element★

63147	$220.00	As/Sb/Bi	Q/N
63116	180.00	As/Ni	Q/N
63148	220.00	As/Se/Te	Q/N
63034	180.00	Ba/Ca/Sr	P/N
63133	210.00	Ba/Ca/Sr/Mg	Q/N
62930	175.00	Ca/Mg/Al	Q/N
63036	180.00	Ca/Mg/Al/Li	Q/N
63207	140.00	Ca/Zn	Q/N
63174	190.00	Cr/Co/Ni	Q/N
63176	250.00	Cr/Co/Cu/Fe/Mn/Ni	Q/N
63208	160.00	Cr/Cu	Q/N
63108	210.00	Cr/Fe/Mn/Ni	Q/N
63190	160.00	Cu/Co	Q/N
63119	180.00	Cu/Ga	Q/N
63132	210.00	Cu/Pb/Zn/Ag	Q/N
63131	130.00	Cu/Mn	Q/N

HOLLOW CATHODE LAMPS, Multi-Element★

63134	$210.00	Cu/Zn/Fe/Mn	Q/N
63146	220.00	Cu/Zn/Pb/Cd	Q/N
63109	210.00	Cu/Zn/Pb/Sn	Q/N
63135	185.00	Cu/Zn/Mo	Q/N
63141	220.00	Cu/Zn/Mo/Co	Q/N
63211	220.00	Au/Cu/Fe/Ni	Q/N
63117	170.00	Au/Ni	Q/N
63118	190.00	In/P	Q/N
63106	185.00	Fe/Cu/Mn	Q/N
63179	240.00	Fe/Cu/Ni/Pb/Zn	Q/N
63171	215.00	Pb/Zn/Ag	Q/N
63177	195.00	Mo/Cu/Fe	Q/N
63130	170.00	Se/Ni	Q/N
63216	210.00	Ag/Zn/Pb/Cd	Q/N
63173	175.00	Na/K	P/N

63490 $ 200.00 H_2 CONTINUUM LAMP SOURCE Q/H

* P = Pyrex Q = Quartz N = Neon A = Argon H = Hydrogen

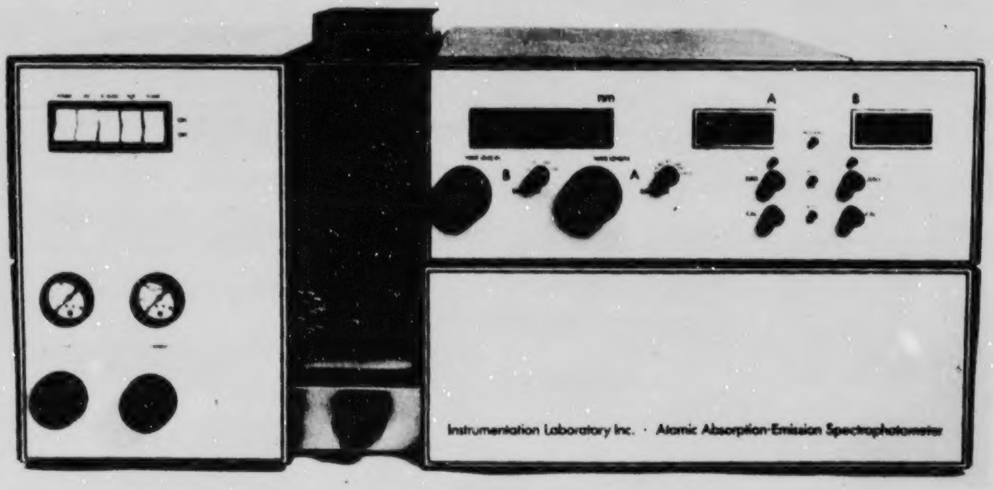
★ Delivery on multi-element lamps is 6-8 weeks; All single element lamps are stock items.

Address

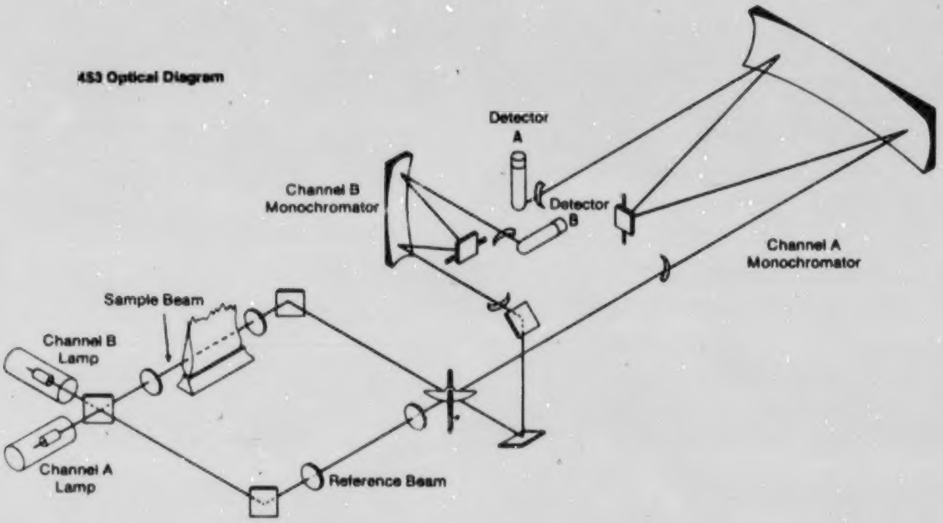
Instrumentation Laboratory, Inc.
Jonspin Road
Wilmington, MA 01887
(617) 658-5125
Attn: Mr. Tom Schulte

Atomic Absorption/Emission Spectrophotometer

Instrumentation Labs, IL 453


nm
A
B
Instrumentation Laboratory Inc. · Atomic Absorption-Emission Spectrophotometer

453 Optical Diagram


Detector
A
Channel B
Monochromator
Detector
B
Channel A
Monochromator
Sample Beam
Channel B
Lamp
Channel A
Lamp
Reference Beam

Class	Laboratory Analysis
Category	Air - Particulates Water - Fresh, Waste, or Saline Biomedical - Blood, Serum, Urine, or Tissue
Principle of Operation	Atomic Absorption/Emission Spectrophotometer: Dual channel, double beam spectrophotometer provides simultaneous determinations in either absorption or emission mode on either channel. Can also use an internal standard for absorption or emission analysis. Has double beam background correction.

Lower Detectable

Dependent on metal, pre-measurement procedure, and mode of atomization. Can be in the picogram range. Allows determination of over sixty-six (66) elements.

TABLE 1

Typical Detection Limits – Atomic Absorption/Emission*

Element	A A	A E	Element	A A	A E
As	0.1	12.0	Ta	3.0	4.0
Ge	14	0.42	V	0.05	0.10
Nb	3.0	1.2	Ga	0.05	0.06
Li	.001	0.00002	Mo	0.03	50
Gd	4.0	0.07	Zn	0.001	8.0
Ce	ND**	100.0	Co	0.002	026
U	40.0	5.0	K	0.003	0.00005
Yb	0.02	0.006	Cd	0.001	0.76
La	2.0	0.014	Cu	0.004	0.01

*Presented in micrograms/milliliter
**Not determined

TABLE 2

Precision of Analyses Utilizing Internal Standards

Element	Matrix	% Relative Standard Deviation	
		Direct	Internal Standard
Fe	Whole Blood	0.49	0.21
Ni	Stainless Steel	0.51	0.18
Mn	Al Alloy	0.83	0.58
Fe	Al Alloy	1.55	0.77
Mg	Al Alloy	0.77	0.43
Ca	Cement	0.79	0.37
Al	Cryolite	1.35	0.61
Au	Au Alloy	0.85	0.22

Range

ppb to ppm

Interferences

Dependent on wavelength used and metal measured, but generally few. Interference can be overcome by addition of corrective reagents.

Multiparameter Capability

Can analyze two (2) elements simultaneously

Sampling

Method: Batch or automatic, sample in solution
Volume: From 1 μl to 3 ml dependent upon atomization source
Rate: Up to 12 determinations per minute

Performance

Electronics: Solid state dual modulated synchronous detection system
Linearity: Varies with element determined
System Stability: Long term 0.1%
Short term 0.005%
Detector: Photomultiplier tube
Readout: Two four-digit digital concentration readouts
Integration: 10, 20 or 40 sec integration times
Scale Expansion: 250x
Other: Auto zero, auto calibrate, and curve correction; six lamp turret with warmup

Channel A Monochromator: 0.33 meter Ebert mount with f/9 aperture
Grating: 32 x 32 mm ruled area; 1200 grooves per mm
Range: 190 to 900 nm
Resolution: 0.03 nm, first order
Reciprocal Linear Dispersion: 25 A/mm first order
Slit System: Curved variable in seven steps from 10 μ to 2000 μ
Wavelength Scan: 5, 20, or 40 nm/min forward or reverse

Channel B Monochromator: 0.16 meter Ebert mount
Grating: 26 x 37 mm ruled area
1200 grooves per min
Range: 190 to 900 nm
Resolution: 0.2 nm, first order
Slit System: Curved variable in four steps from 25 μ to 450 μ
Wavelength Scan: None

Gas Control: Fully automatic system with sensors for gas supply pressure and burnerheads, and a UV flame monitor. Automatic conversion to N_2O/C_2H_2 from Air/C_2H_2
Gas Combination: Air/C_2H_2, N_2O/C_2H_2, Ar/H_2/E.A., Air/H_2
Venting: Minimum diameter, 4"
Minimum opening, 9"
Minimum exhaust capacity, 100 cfm

Operation

Procedure: Pre-installation handbook and customer engineer provided
Maintenance: Field service engineers available
Training: Available on request, five-day seminar available at no tuition

Requirements

Power: 115 Vac, nominal ±10%, 2 amps, 60 Hz, other options
Weight: Bench - 96.5 kg (212 lb)
Shipping - 127.5 kg (280 lb)
Dimensions: 48.5 cm H, 103 cm L, 51 cm D (19" x 40.5" x 20")

Features

Output: Recorder nominally 100 mV
Options: Reference Filters from 248.3 to 766.5 nm, Gas Control Equipment, Burners, Hollow Cathode Lamps, Standards, Recorders

References

Manufacturer's Specifications

Cost

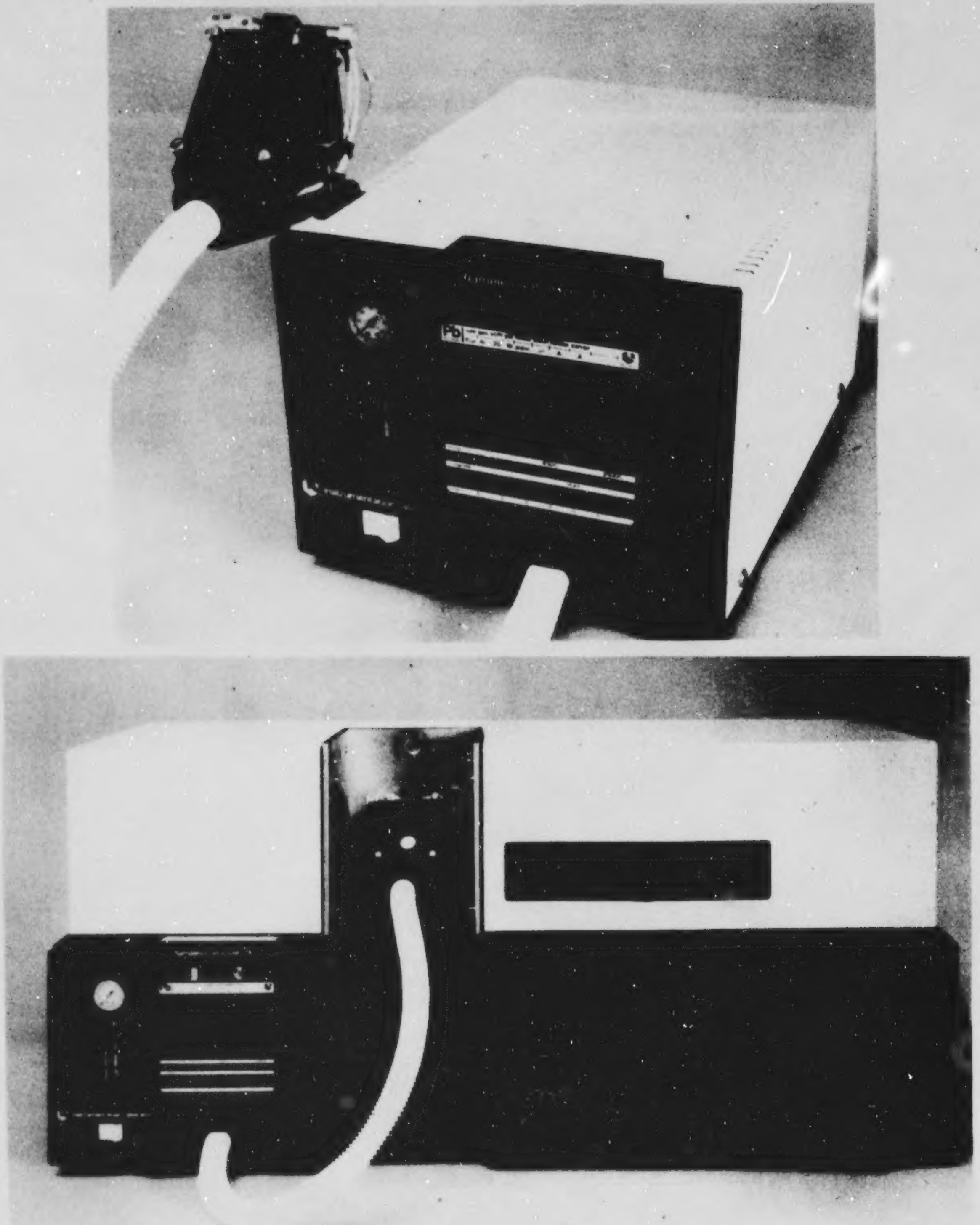
Model 453	$14,000	As described above
Model 353	$12,500	Dual channel, double beam with interference filter mono in B channel
Model 253-02	$11,000	Single channel, double beam with turret and background correction
Model 253-01	$10,000	Single channel, double beam with turret
Model 253	$ 9,500	Single channel, double beam

Address

Instrumentation Laboratory, Inc.
Jonspin Road
Wilmington, MA 01887
(617) 658-5125
Attn: Mr. Tom Schulte

Flameless Atomic Absorption

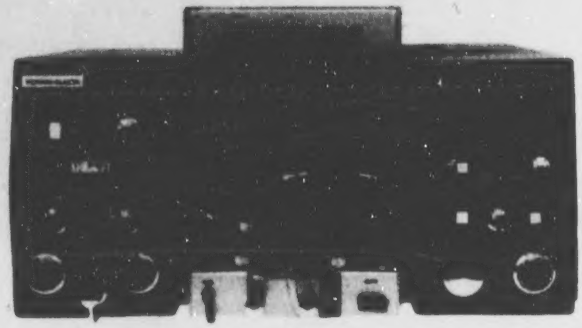
Instrumentation Labs, Model IL 455



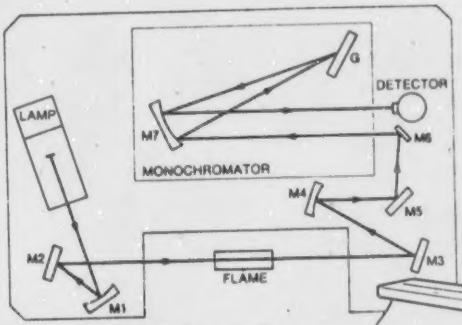
Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Flameless Atomic Absorption Sampler: A furnace cell and temperature programmable atomization device to replace flame assembly. Furnace cell accepts pyrolytic graphite or tungsten cuvettes having round or rectangular cross section geometries. Inert purge gas system, six-step multi-linear temperature programming up to 3500°C.
Lower Detectable Limit	
Range	
Interferences	
Multiparameter Capability	
Sampling	Method: Batch and semi-automatic Volume: 1 µl to 80 µl Capacity: Temperature Control: Ramp or instantaneous heating in each step, 45 sec. max. time in each step. Cuvettes: Graphite or tungsten Round cross section, 4.75 mm x 38 mm long, I.D. Rectangular cross section; 4.75 mm x 4.75 mm x 38 mm long, I.D. Lifetime; 50-1000 shots, depending on temperature levels selected
Performance	Electronics: Linearity: Stability: Scale Expansion:
Operation	Calibration: Procedure: Training: Unattended Period: Maintenance: Temperature Compensation:
Requirements	Power: 220 V ± 10%, 50/60 Hz, 15 amps Weight: 45.5 kg (100 lb) Dimensions: Furnace cell, 8 x 13 x 10 cm Programmer, 49 x 28 x 32 cm Cooling water: 0.5 to 1 liter/min at 3500°C
Features	UV transmitting quartz cell windows. Automatic control of cell access door. Printed overlay temperature program cards. Meter readout of measured temperature from 25°C to 3500°C with automatic ranging. Cell pressurization and auto clean selectable at operator command. Purge gas (argon) flow indicated from 0 to 30 SCHF; cell pressure indication from 0 to 60 psig in pressurization mode.
References	Manufacturer's Bulletin
Cost	Model IL 455 $4,350.
Address	Instrumentation Laboratory, Inc. 113 Hartwell Avenue Lexington, MA 02173 ATTN: Ms. R. Sovie (617) 861-0710

Atomic Absorption Spectrophotometer

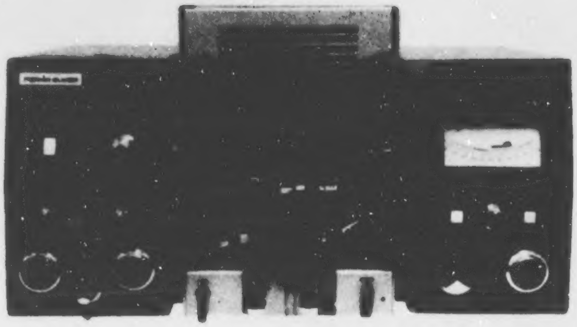
Perkin-Elmer, Model 103 and 107



Model 107

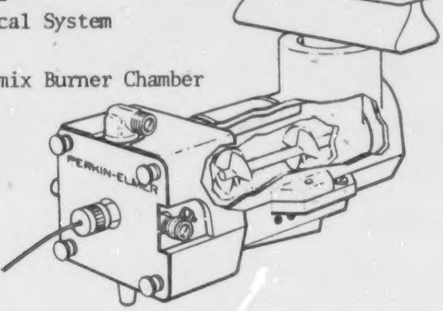


Mirror Optical System



Model 103

Premix Burner Chamber



Class	Laboratory
Category	Air: Particulates Water: Fresh, Waste, or Saline Biomedical: Blood, Serum, Urine, or Tissue
Principle of Operation	Atomic Absorption Spectrophotometer: Single beam, all-mirror optical system, premix burner chamber, 3d adjustable burner position, electric flame ignition system, auto-zero circuit, signal integration mode, and calibration circuit.

Lower Detectable Limit

Models 103/107 Atomic Absorption Detection Limits

Element	µg/ml	Element	µg/ml	Element	µg/ml	Element	µg/ml
Aluminum[1]	0.02	Gallium	0.05[1]	Nickel	0.02	Sodium	<0.001
Antimony	0.07	Germanium[1]	0.8	Niobium[1,3]	3.	Strontium[4]	0.004
Arsenic[2]	0.25	Gold	0.03	Osmium[1]	0.2	Tantalum[1]	6.
Barium[1,3]	0.03	Hafnium[1]	2.	Palladium	0.025	Tellurium	0.1
Beryllium[1]	0.002	Holmium[1,3]	0.1	Phosphorus[1]	100.	Terbium[1,3]	0.8
Bismuth	0.1	Indium	0.03	Platinum	0.07	Thallium	0.07
Boron[1]	2.5	Iridium	1.2	Potassium	0.004	Thulium[1,3]	0.025
Cadmium	0.002	Iron	0.01	Praseodymium[1,3]	10.	Tin[2]	0.02
Calcium	0.002	Lanthanum[1,3]	7.	Rhenium[1]	0.7	Titanium[1]	0.15
Cesium	0.005[3,4]	Lead	0.03	Rhodium	0.01	Tungsten[1]	2.2
Chromium	0.008	Lithium	0.0025	Rubidium	0.002[4]	Uranium[1]	80.
Cobalt	0.015	Lutetium[1,3]	0.7	Ruthenium	0.08	Vanadium[1]	0.16
Copper	0.005	Magnesium	0.0001	Samarium[1,3]	3.	Ytterbium[1,3]	0.01
Dysprosium[1,3]	0.2	Manganese	0.008	Scandium[1,3]	0.03	Yttrium[1,3]	0.12
Erbium[1,3]	0.07	Mercury	1.	Selenium[2]	0.08	Zinc	0.003
Europium[1,3]	0.1	Molybdenum[1]	0.02	Silicon[1]	0.2	Zirconium[1]	2.
Gadolinium[1,3]	2.	Neodymium[1,3]	5.	Silver	0.002		

1) Nitrous oxide-acetylene flame 2) Argon-hydrogen-entrained air flame 3) 1000 µg/ml K to control ionization 4) Flame emission with air-acetylene flame

Range

10^8 crders of magnitude: from 10^{-4} to 10^4 µg/ml, depending upon element and wavelength

Interferences

Minimal for most analysis. Interference can be overcome by carefully selecting the proper flame conditions or using chemical interference suppressants in the sample.

Multiparameter Capability

68 single-element lamps, 17 multi-element lamps

Sampling

Method: Batch or automated
Sample Area: 20 cm W, 15 cm D
Capacity: Up to 10 samples per minute
Volume: 1 ml typical; less than 10 µl with accessory sampling devices

Performance

Electronics:

Linearity:
Stability:
Scale Expansion: 1 to 50 X
Damping: 3 switch-selectable positions
Detector: Photomultiplier with S-5 cathode
Integration Times: 3 and 10 seconds

Monochromator: Littrow grating system, 267 mm focal length

Grating: 64 × 64 mm, 1800 lines/mm blazed at 220 nm
Dispersion: 1.6 nm/mm
Range: 190 - 870 nm
Spectral Bandpass: 0.2, 0.7, 2 nm

Gas Control: Integral controls, containing individual needle valve, flow controls for fuel and oxidant. Automatic ignition. 3-way oxidant selection valve with safety interlock.

Oxidant: Air or N_2O
Fuel: C_2H_2 or H_2
Venting: Recommended at 300 cfm

Operation

Calibration: With standardized solutions; readout in concentration
Procedure: Aspiration of solution, readout in concentration on meter (Model 103) or digits (Model 107)
Maintenance: Minimal
Training Required: Moderate

Requirements

Power: 105 - 125 or 200 - 240 V, 50 or 60 Hz, 200 Watts
Weight: 35 kg (80 lb) net, 65 kg (150 lb) gross
Dimensions: 63 cm W, 38 cm D, 29 cm H (24.5" W, 15" D, 11.5" H)

Features

Single beam optics
Premix burner chamber
Automatic flame ignition
Meter readout (Model 103) or 4-digit bipolar readout (Model 107)
Readout in absorbance, concentration, or emission intensity
Auto zero
Signal integration
Flame emission standard

Options

Graphite furnace sampling system, HGA 2100	$4,290
A.A. microsampling system	650
Flameless mercury analysis system	550
As/Se sampling system	425
Auto 200 automated sampling system	3,500
Recorder Model 056, 10mV	1,450
Printer sequencer	2,450
Typewriter readout assembly	5,500
Universal Digital Readout accessory with peak reader	1,250

References

Manufacturer's specifications

Cost

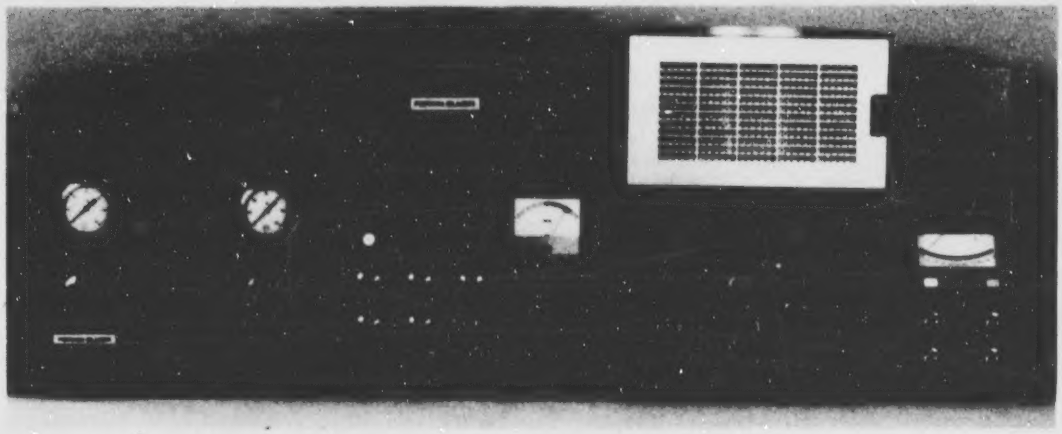
Model 103	$4,900
Model 107	5,500

Address

Perkin-Elmer Corporation
Instrument Division
Norwalk, CT 06856
(203) 762-1000

Atomic Absorption Spectrophotometer

Perkin-Elmer, Model 305B



Class	Laboratory
Category	Air: Particulate Water: Fresh, Waste or Saline Biomedical: Blood, Serum, Urine, or Tissue
Principle of Operation	Atomic absorption spectrophotometer, double beam, premix burner chambers, electric flame ignition, digital readout
Lower Detectable Limit	

Table 1: Detection Limits for the Model 305B
Element and Detection Limit in μg/ml

Element	Detection Limit
Aluminum[1]	0.03
Antimony	0.1
Arsenic[2] [4]	0.1
Barium[1] [4]	0.02
Beryllium[1]	0.001
Bismuth	0.04
Boron[1]	2.5
Cadmium	0.001
Calcium	0.001
Cesium	0.05
Chromium	0.003
Cobalt	0.01
Copper	0.002
Dysprosium[1]	0.2
Erbium[1]	0.1
Europium[1]	0.04
Gadolinium[1]	4.0
Gallium	0.1
Germanium[1]	1.0
Gold	0.02
Hafnium[1]	8.0
Holmium[1]	0.1
Indium	0.05
Iridium	2.0
Iron	0.01
Lanthanum[1]	2.0
Lead	0.02
Lithium	0.0006
Lutetium[1]	3.0
Magnesium	0.0001
Manganese	0.002
Mercury	0.5
Molybdenum[1] [4]	0.03
Neodymium[1]	2.0
Nickel	0.01
Niobium[1]	1.0
Osmium[1]	0.5
Palladium	0.02
Phosphorus[1]	100
Platinum	0.1
Potassium	0.005
Praseodymium[1]	10.0
Rhenium[1]	1.0
Rhodium	0.03
Rubidium	0.005
Ruthenium	0.3
Samarium[2]	2.0
Scandium[1]	0.1
Selenium[2] [4]	0.1
Silicon[1]	0.08
Silver	0.002
Sodium	0.002
Strontium[1] [4]	0.01
Tantalum[1]	2.0
Tellurium	0.09
Terbium[1]	3.0
Thallium	0.03
Thulium[1]	0.2
Tin[2] [4]	0.02
Titanium[1]	0.09
Tungsten[1]	3.0
Uranium[1]	30.0
Vanadium[1]	0.06
Ytterbium[1]	0.04
Yttrium[1]	0.3
Zinc	0.002
Zirconium[1]	5.0

[1] Nitrous Oxide Flame
[2] Argon-Hydrogen-Air Diffusion Flame
[3] Air-Hydrogen Flame
[4] Can also be determined in the Air-Acetylene Flame

These detection limits were obtained with the aid of the TR-1 typewriter readout unit and a time-sharing computer system.

Range
10^8 orders of magnitude: from 10^{-4} to 10^4 µg/ml, depending upon element and wavelength

Interferences
Most interferences can be overcome by carefully selecting the proper flame conditions, using chemical interference suppressants in the sample, or optional Deuterium Background Corrector.

Multiparameter Capability
68 single-element lamps, 17 multi-element lamps

Sampling
Method: Batch or automated
Sample area: 20cm W, 15 cm D
Capacity: Up to 10 samples per minute
Volume: 1 ml typical; less than 10 µl with accessory sampling devices

Performance
Electronics:

Linearity:
Stability:
Scale Expansion: 0.3 to 50X
Damping: 4 switch-selectable positions
Detector: Photomultiplier with S-20 cathode
Integration Times: 2 and 10 seconds

Monochromator: Czerny-Turner system, 400 mm focal length
Grating: UV, 64 x 64 mm, 2880 lines/mm blazed at 210 nm
VIS, 64 x 64 mm, 1440 lines/mm blazed at 580 nm
Dispersion: UV, 0.65 nm/mm
VIS, 1.3 nm/mm
Range: 180 to 900 nm
Spectral Bandpass: UV, 0.03, 0.07, 0.2, 0.7, 2.0, 7.0 nm
VIS, 0.05, 0.14, 0.40, 1.4, 4.0, 14 nm

Gas Control: Separate control box, containing individual controls and meters for oxidant and fuel pressure and flow. Pushbutton actuated remote flame ignition. N_2O safety interlock.

Oxidant: Air or N_2O
Fuel: C_2H_2 or H_2
Venting: Recommended at 300 CFM

Operation
Calibration: With standardized solutions, readout in concentration
Procedure: Aspiration of solution, readout of concentration on meter
Maintenance: Minimal
Training Required: Moderate

Requirements:
Power: 105-125 or 200-240 V, 50 or 60 Hz, 200 Watts
Weight: 75 kg net, 130 kg gross
Dimensions: 45 cm H, 61 cm D, 89 cm W

Features
Double beam optics
Premix burner chamber
Pushbutton flame ignition
Readout in absorbance, concentration, or emission intensity
Auto zero
Meter Readout
Signal integration
Curvature correction
Flame emission standard

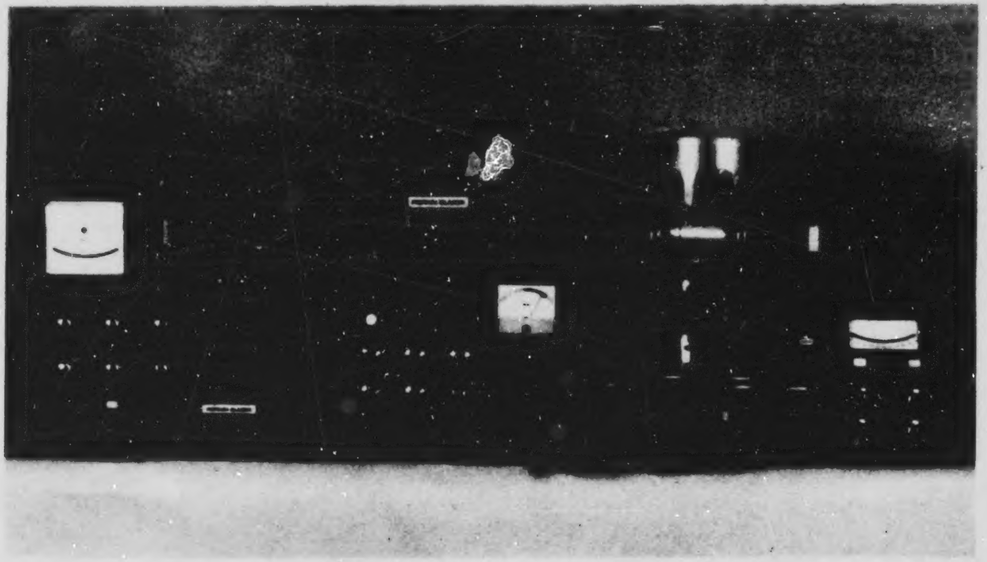
Options	Graphite furnace sampling system	$ 4,290
	A.A. microsampling system	650
	Flameless Mercury analysis system	550
	High sensitivity As/Se sampling system	425
	Auto 200 automated sampling system	3,500
	Deuterium background corrector	
	Printer sequencer	2,450
	Typewriter readout assembly	5,500
	Recorder	1,450
	Wavelength drive assembly	
	Universal digital readout accessory with peak reader	1,250
References	Manufacturers Specifications	
Cost	Model 305B	$8,950

Address

Perkin-Elmer Corporation
Instrument Division
Norwalk, CT 06856
(203) 762-1000

Atomic Absorption Spectrophotometer

Perkin-Elmer, Model 305BG



Class	Laboratory
Category	Air: Particulates Water: Fresh, Waste, or Saline Biomedical: Blood, Serum, Urine or Tissue
Principle of Operation	Atomic Absorption Spectrophotometer: Double beam, flameless graphite furnace, deuterium background corrector, auto-zero circuit, recorder read-out. Designed for use with accessory HGA Graphite Furnace.
Lower Detectable Limit	

TABLE I: DETECTION LIMITS FOR THE HGA (in μg/ml)

	HGA*		HGA*		HGA*
Aluminum	0.00003	Iridium		Ruthenium	
Antimony	0.0002	Iron	0.00003	Samarium	
Arsenic		Lanthanum		Scandium	
Barium		Lead	0.00006	Selenium	
Beryllium		Lithium		Silicon	0.00008
Bismuth	0.0001	Lutetium		Silver	0.0000025
Boron		Magnesium		Sodium	
Cadmium	0.000001	Manganese	0.00001	Strontium	
Calcium		Mercury		Tantalum	
Cesium		Molybdenum		Tellurium	
Chromium	0.00005	Neodymium		Terbium	
Cobalt	0.00004	Nickel	0.0001	Thallium	0.00014
Copper	0.00001	Niobium		Thulium	
Dysprosium		Osmium		Tin	
Erbium		Palladium		Titanium	
Europium		Phosphorus		Tungsten	
Gadolinium		Platinum		Uranium	
Gallium		Potassium		Vanadium	
Germanium		Praseodymium		Ytterbium	
Gold	0.00008	Rhenium		Yttrium	
Hafnium		Rhodium		Zinc	0.00000
Holmium		Rubidium		Zirconium	
Indium					

* *Most elements determined with flame sampling can also be determined wi the HGA, although detection limits for all elements determinable with t Furnace are not given here.*

Range

10^9 orders of magnitude: from 10^{-6} to 10^3 μg/ml, depending upon element and wavelength

Interferences

Minimal for most analysis. Interference can be overcome by proper choice of operating parameters or use of Deuterium Background Corrector.

Multiparameter Capability

68 single-element lamps, 17 multi-element lamps

Sampling

Method: Batch
Sample Area: 20 cm W, 15 cm D
Capacity: Up to 60 samples per hour
Volume: Maximum of 100 μl

Performance

Electronics:

Linearity:
Stability:
Scale Expansion: 0.3 to 50 X
Damping: 4 switch-selectable positions
Detector: Photomultiplier with S-20 cathode
Integration Times: 2 and 10 seconds

Monochromator: Czerny-Turner system, 400 mm focal length

Grating: UV, 64 × 64 mm, 2880 lines/mm blazed at 210 nm
VIS, 64 × 64 mm, 1440 lines/mm blazed at 580 nm
Dispersion: UV -- 0.65 nm/mm
VIS -- 1.3 nm/mm
Range: 180 to 900 nm
Spectral Bandpass: UV -- 0.03, 0.07, 0.2, 0.7, 2.0, 7.0 nm
VIS -- 0.05, 0.14, 0.40, 1.4, 4.0, 14 nm
Oxidant: Air for N_2O
Fuel: C_2H_2 or H_2
Venting: Recommended at 300 cfm

Operation

Calibration: With standardized solutions; readout in concentration
Procedure: Introduction of sample, readout on optional recorder or Universal Digital Readout with peak reader
Maintenance: Minimal
Training Required: Moderate

Requirements

Power: 105-125 or 200-240 V, 50 or 60 Hz/ 200 Watts
Weight: 75 kg net, 130 kg gross
Dimensions: 45 cm H, 61 cm D, 89 cm W

Features

Double beam optics
Premix burner chamber
Pushbutton flame ignition
Readout in absorbance, concentration, or emission intensity
Deuterium Background Corrector
Auto zero
Meter readout
Signal integration
Curvature correction
Flame emission standard

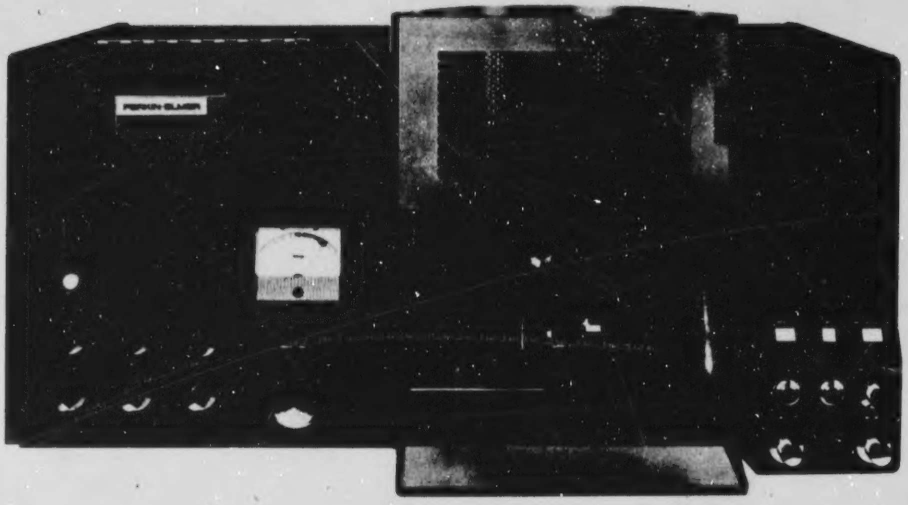
Options

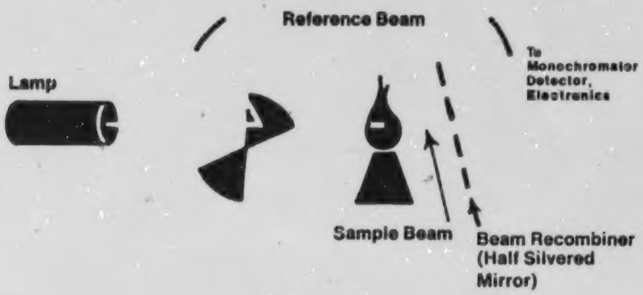
Graphite furnace sampling system	$ 4,290
A.A. microsampling system	650
Flameless mercury analysis system	550
High sensitivity As/Se sampling system	425
Auto 200 automated sampling system	3,500
Deuterium background corrector	
Printer sequencer	2,450
Typewriter readout assembly	5,500
Recorder	1,450
Wavelength drive assembly	

References	Manufacturer's specifications	
Cost	Model 305BG	$8,950.
Address	Perkin-Elmer Corporation Instrument Division Norwalk, CT 06856 (203) 762-1000	

Atomic Absorption Spectrophotometer

Perkin-Elmer, Model 306


PERKIN-ELMER


Reference Beam
Lamp
To Monochromator Detector, Electronics
Sample Beam
Beam Recombiner (Half Silvered Mirror)

***Double-beam optical system.** Light from lamp is passed alternately through and past flame. Electronics produce ratio of sample to reference beams.*

Class	Laboratory
Category	Air: Particulates Water: Fresh, Waste or Saline Biomedical: Blood, Serum, Urine, or Tissue
Principle of Operation	Atomic Absorption Spectrophotometer: Double beam optical system, premix burner chamber, electric flame ignition, auto-zero and auto calibration circuits, signal integration mode, and digital read-out.

Lower Detectable Limit

TABLE I: DETECTION LIMITS FOR THE MODEL 306

ELEMENT AND DETECTION LIMIT IN μg/ml

Aluminum[1]	0.03	Iridium	2.0	Ruthenium	0.3
Antimony	0.1	Iron	0.01	Samarium[2]	2.0
Arsenic[2,4]	0.1	Lanthanum[1]	2.0	Scandium[1]	0.1
Barium[1,4]	0.02	Lead	0.02	Selenium[2,4]	0.1
Beryllium[1]	0.001	Lithium	0.0006	Silicon[1]	0.08
Bismuth	0.04	Lutetium[1]	3.0	Silver	0.002
Boron[1]	2.5	Magnesium	0.0001	Sodium	0.002
Cadmium	0.001	Manganese	0.002	Strontium[1,4]	0.01
Calcium	0.001	Mercury	0.5	Tantalum[1]	2.0
Cesium	0.05	Molybdenum[1,4]	0.03	Tellurium	0.09
Chromium	0.003	Neodymium[1]	2.0	Terbium[1]	3.0
Cobalt	0.01	Nickel	0.01	Thallium	0.03
Copper	0.002	Niobium[1]	1.0	Thulium[1]	0.2
Dysprosium[1]	0.2	Osmium[1]	0.5	Tin[2,4]	0.02
Erbium[1]	0.1	Palladium	0.02	Titanium[1]	0.09
Europium[1]	0.04	Phosphorus[1]	100	Tungsten[1]	3.0
Gadolinium[1]	4.0	Platinum	0.1	Uranium[1]	30.0
Gallium	0.1	Potassium	0.005	Vanadium[1]	0.06
Germanium[1]	1.0	Praseodymium[1]	10.0	Ytterbium[1]	0.04
Gold	0.02	Rhenium[1]	1.0	Yttrium[1]	0.3
Hafnium[1]	8.0	Rhodium	0.03	Zinc	0.002
Halmium[1]	0.1	Rubidium	0.005	Zirconium[1]	5.0
Indium	0.05				

[1] *Nitrous Oxide Flame*
[2] *Argon-Hydrogen-Air Diffusion Flame*
[3] *Air-Hydrogen Flame*
[4] *Can also be determined in the Air-Acetylene Flame*

These detection limits were obtained with the aid of the TR-1 typewriter readout unit and a time-sharing computer system. They are, therefore, objective, not subjective. (For description of computer method, see Reprint AA-569).

Range

10^{8} orders of magnitude: from 10^{-4} to 10^{4} μg/ml, depending upon element and wavelength

Interferences

Minimal for most analysis. Interference can be overcome by carefully selecting the proper flame conditions, using chemical interference suppresants in the sample, or optional Deuterium Background Corrector.

Multiparameter Capability

68 single-element lamps, 17 multi-element lamps

Sampling

Method: Batch or automated
Sample Area: 20 cm W, 15 cm D
Capacity: Up to 10 samples per minute
Volume: 1 ml typical; less than 10 μl with accessory sampling devices

Performance

Electronics:

Linearity:
Stability:
Scale Expansion: 1.0 to 100 X
Damping: 4 switch-selectable positions
Detector: Photomultiplier with S-20 cathode
Integration Times: 0.1, 2 and 10 seconds

Performance (Cont'd)

Monochromator: Czerny-Turner system, 400 mm focal length
Grating: UV -- 64 × 64 mm, 2880 lines/mm blazed at 210 nm
VIS - 64 × 64 mm, 1440 lines/mm blazed at 580 nm
Dispersion: UV -- 0.65 nm/mm
VIS -- 1.3 nm/mm
Range: 180 to 900 nm
Spectral Bandpass: UV -- 0.03, 0.07, 0.2, 0.7, 2.0, 7.0 nm
VIS -- 0.05, 0.14, 0.40, 1.4, 4.0, 14 nm

Gas Control: Separate control box, containing individual controls and meters for oxidant and fuel pressure and flow. Pushbutton actuated remote flame ignition. N_2O safety interlock.

Oxidant: Air or N_2O
Fuel: C_2H_2 or H_2
Venting: Recommended at 300 cfm

Operation

Calibration: Automatic with standardized solutions; readout in concentration
Procedure: Aspiration of solution, readout of concentration in digits
Maintenance: Minimal
Training Required: Moderate

Requirements

Power: 105-125 or 200-240 V, 50 or 60 Hz, 200 Watts
Weight: 75 kg net, 130 kg gross
Dimensions: 45 cm H, 61 cm D, 89 cm W

Features

- Double beam optics
- Premix burner chamber
- Pushbutton flame ignition
- Four-digit bipolar readout
- Readout in absorbance, concentration, or emission intensity
- Auto calibration
- Auto zero
- Signal integration
- Curvature correction
- Flame emission standard

Options

Graphite furnace sampling system	$4,290
A.A. microsampling system	650
Flameless Mercury analysis system	550
High sensitivity As/Se sampling system	425
Auto 200 automated sampling system	3,500
Deuterium background corrector	
Printer sequencer	2,450
Typewriter readout assembly	5,500
Recorder	1,450
Wavelength drive assembly	

References

Manufacturer's specifications

Cost

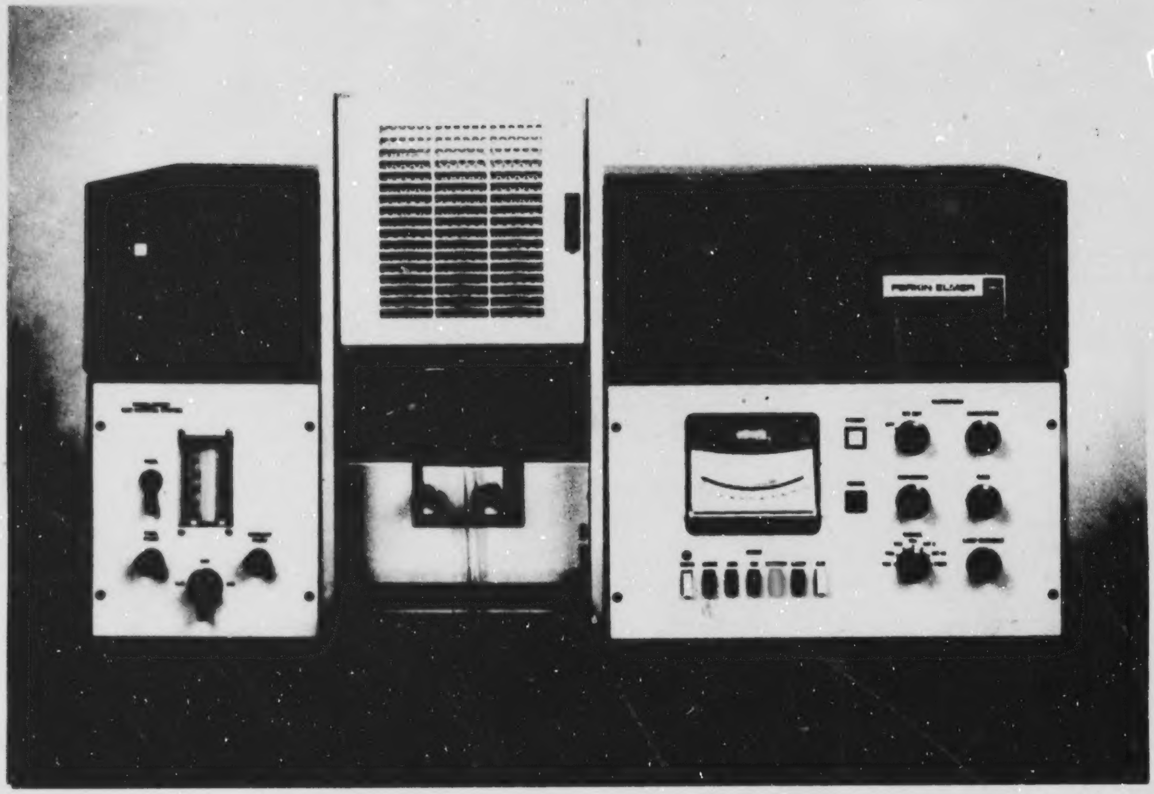
Model 306 $9,990.

Address

Perkin-Elmer Corporation
Instrument Division
Norwalk, CT 06856
(203) 762-1000

Atomic Absorption Spectrophotometer

Perkin-Elmer Model 360



Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Atomic absorption, double beam, mechanical chopper, electronic phasing regulator, graphite furnace sampler option, curvature correction circuit, automatic gain control, integrator, peak height and peak area, auto zero, D_2 background correction, electronic intensity control of D_2 and light source, electric flame ignition, interlocked flame control option

Lower Detectable Limits

MODEL 360 DETECTION LIMITS

Element	DL (μg/ml)	Element	DL (μg/ml)
Ag	0.002	Mn	0.003
Al*	0.02	Mo*	0.02
As (EDL)	0.4[a]	Na	0.0005
Au	0.02	Ni	0.01
B*	2.	Pb (EDL)	0.015
Ba*	0.02	Rb (FE)	0.0005
Be*	0.002	Sb (EDL)	0.03
Bi (EDL)	0.03	Se (EDL)	0.25[a]
Ca	0.002	Si*	0.1
Cd (EDL)	0.0015	Sn*(EDL)	0.07
Co	0.015	Sr	0.001
Cr	0.003	Te (EDL)	0.07
Cu	0.002	Ti*	0.08
Fe	0.01	Tl (EDL)	0.03
Hg	0.2	V*	0.05
K	0.001	W*	2.
Li	0.002	Zn	0.001
Mg	0.00005	Zr	1.

* = nitrous oxide-acetylene flame (air-acetylene used for all other detection limits)

a = detection limit may be improved with use of simultaneous background correction

Range

Absorbance: 0-2
Concentration: 10^{-4} to 10^{4} μg/ml depending on element and wavelength
Flame Emission: 10^{-4} to 10^{4} μg/ml depending on element and wavelength
Energy (Transmission): Automatically set

Interferences

Most interferences can be overcome by carefully selecting the proper flame conditions, using chemical interference suppressants in the sample, or optional Deuterium Background Corrector.

Multiparameter Capability

68 single element lamps, 17 multielement lamps

Sampling

Method: Batch or automatic
Volume: 1 ml typical; less than 10 μl with accessory sampling devices
Capacity: 10 samples/minute
Pathlength: 100 mm with air/C_2H_2; 50 mm with N_2O/C_2H_2

Performance

Electronics: Solid state
Linearity: Better than 1%
Stability: Better than 0.1%
Scale Expansion: 0.5 to 50x
Light Source: Hollow cathode lamps, D_2 arc correlation (optional)
Detector: Multialkali photomultiplier
Integrator: 3 and 10 seconds

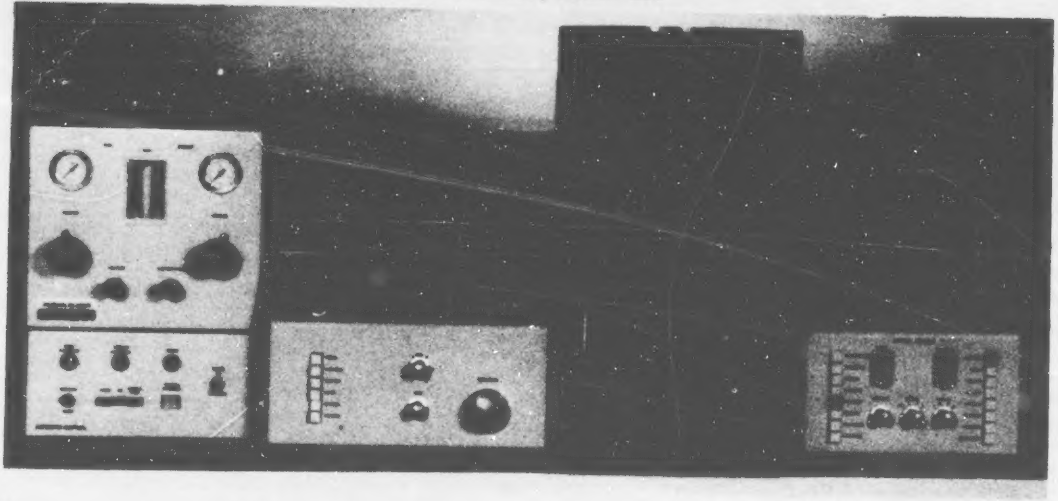
Monochromator:
Grating: 64 x 64 mm, 1880 lines/mm blazed at 220 nm
Wavelength Range: 190 to 900 nm
Wavelength Accuracy: ±0.4 nm
Wavelength Repeatability: ±0.1 nm
Resolution: 0.2 nm
Reciprocal Dispersion: 2 nm/mm at 250 nm
Slit Width: Two sets of slits, 0.2, 0.7, 2.0 nm bandpass
Stray Light: Negligible

Gas Control: Independent flow meters, flow control, gas interlock (optional)
Fuel: Acetylene or hydrogen
Oxidant: Air or nitrous oxide
Vent: Recommended at 300 CFM

Operation	Calibration: Standard samples, readout in concentration Procedure: Manual provided Training: Two-day training course included in price Unattended Period: Not recommended Maintenance: Service centers in the U.S. Warm-up Time: 10 seconds at turn on	
Requirements	Power: 105-125 or 200-240 volts, 50/60 Hz, 150 watts Weight: 70 kg net, 125 kg gross Dimensions: 40 cm high, 50 cm deep, 88 cm wide	
Features	Output: Tiltable analog meter; recorder connection, DVM optional	
	Options: Digital Display, UDR-3	$ 750
	Recorder (0-10 mV, 6 speeds)	1,450
	Deuterium Arc and Wavelength Scanner	1,550
References	Manufacturer's Bulletin	
Cost	Model 360	6,750
Address	Perkin-Elmer Instrument Division Norwalk, CT 06856 (203) 762-1000	

Atomic Absorption Spectrophotometer

Perkin-Elmer, Model 503



Class Laboratory

Category Air: Particulates
Water: Fresh, Waste or Saline
Biomedical: Blood, Serum, Urine, or Tissue

Principle of Operation Atomic absorption spectrophotometer

Lower Detectable Limit

Table 1: Detection Limits for the Model 503
Element and Detection Limit in μg/ml

Aluminum[1]	0.03
Antimony	0.1
Arsenic[2,4]	0.1
Barium[1,4]	0.02
Beryllium[1]	0.001
Bismuth	0.04
Boron[1]	2.5
Cadmium	0.001
Calcium	0.001
Cesium	0.05
Chromium	0.003
Cobalt	0.01
Copper	0.002
Dysprosium[1]	0.2
Erbium[1]	0.1
Europium[1]	0.04
Gadolinium[1]	4.0
Gallium	0.1
Germanium[1]	1.0
Gold	0.02
Hafnium[1]	8.0
Holmium[1]	0.1
Indium	0.05
Iridium	2.0
Iron	0.01
Lanthanum[1]	2.0
Lead	0.02
Lithium	0.0006
Lutetium[1]	3.0
Magnesium	0.0001
Manganese	0.002
Mercury	0.5
Molybdenum[1,4]	0.03
Neodymium[1]	2.0
Nickel	0.01
Niobium[1]	1.0
Osmium[1]	0.5
Palladium	0.02
Phosphorus[1]	100
Platinum	0.1
Potassium	0.005
Praseodymium[1]	10.0
Rhenium[1]	1.0
Rhodium	0.03
Rubidium	0.005
Ruthenium	0.3
Samarium[2]	2.0
Scandium[1]	0.1
Selenium[2,4]	0.1
Silicon[1]	0.08
Silver	0.002
Sodium	0.002
Strontium[1,4]	0.01
Tantalum[1]	2.0
Tellurium	0.09
Terbium[1]	3.0
Thallium	0.03
Thulium[1]	0.2
Tin[2,4]	0.02
Titanium[1]	0.09
Tungsten[1]	3.0
Uranium[1]	30.0
Vanadium[1]	0.06
Ytterbium[1]	0.04
Yttrium[1]	0.3
Zinc	0.002
Zirconium[1]	5.0

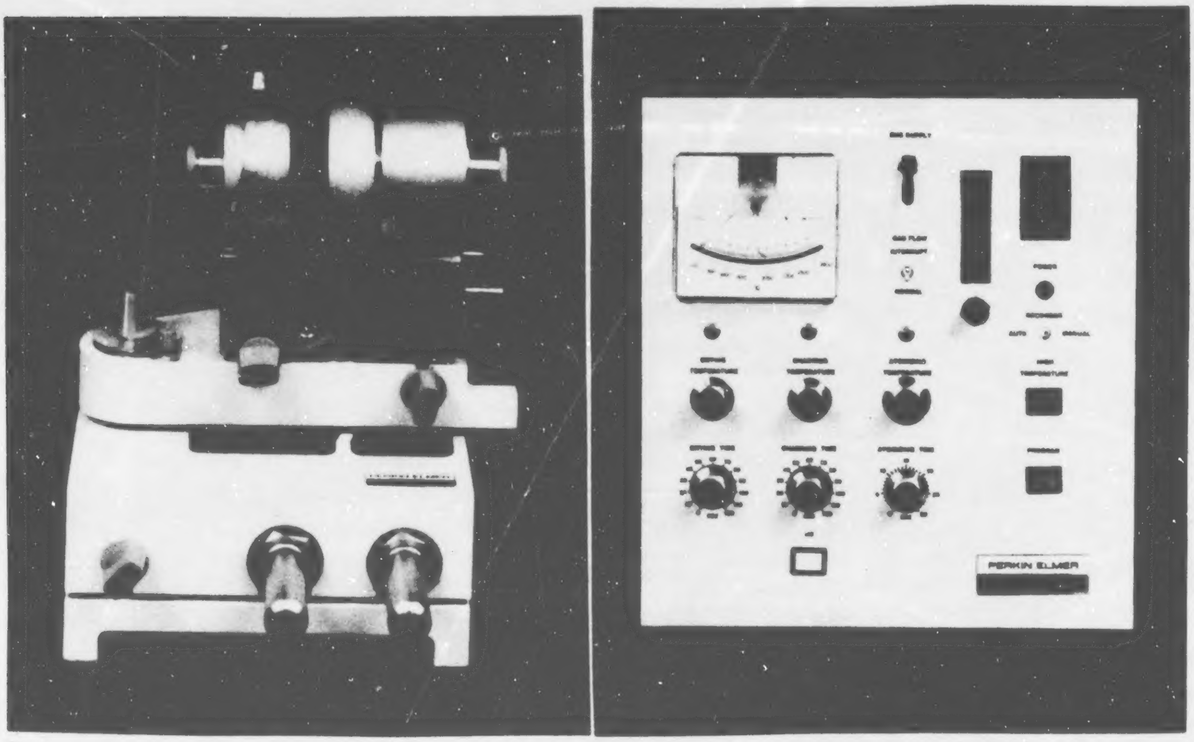
[1] Nitrous Oxide Flame
[2] Argon-Hydrogen-Air Diffusion Flame
[3] Air-Hydrogen Flame
[4] Can also be determined in the Air-Acetylene Flame

These detection limits were obtained with the aid of the TR-1 typewriter readout unit and a time-sharing computer system.

Range	10^8 orders of magnitude: from 10^{-4} to 10^4 μg/ml, depending upon element and wavelength
Interferences	Minimal for most analysis. Interference can be overcome by carefully selecting the proper flame conditions, using chemical interference suppressants in the sample, or optional Deuterium Background Corrector.
Multiparameter Capability	68 single-element lamps, 17 multi-element lamps
Sampling	Method: Batch or automated Sample area: 20 cm W, 15 cm D Capacity: Up to 10 samples per minute Volume: 1 ml typical; less than 10 μl with accessory sampling devices
Performance	Electronics: Linearity: Stability: Scale Expansion: 0.1 to 100X Damping: 4 switch-selectable positions Detector: Photomultiplier with S-20 cathode Integration Times: 0.1, 1, 3 and 10 seconds Monochromator: Czerny-Turner system, 400 mm focal length Grating: UV, 64 x 64 mm, 2880 lines/mm blazed at 210 nm VIS, 64 x 64 mm, 1440 lines/mm blazed at 580 nm Dispersion: UV, 0.65 nm/mm VIS, 1.3 nm/mm Range: 180 to 900 nm Spectral Bandpass: UV, 0.03, 0.07, 0.2, 0.7, 2.0, 7.0 nm VIS, 0.05, 0.14, 0.40, 1.4, 4.0, 14 nm Gas Control: Separate control box, containing individual controls and meters for oxidant and fuel pressure and flow. Pushbutton actuated remote flame ignition. N_2O safety interlock. Flame and pressure sensing safety devices, burner head safety interlock system, automatic switching to N_2O. Oxidant: Air or N_2O Fuel: C_2H_2 or H_2 Venting: Recommended at 300 CFM
Operation	Calibration: Automatic with standardized solutions; readout in concentration Procedure: Aspiration of solution, readout of concentration in digits Maintenance: Minimal Training Required: Moderate
Requirements	Power: 105-125 or 200-240 V, 50 or 60 Hz, 200 Watts Weight: 90 kg net, 145 kg gross Dimensions: 62 cm H, 66 cm D, 110 cm W
Features	Double beam optics Premix burner chamber Pushbutton flame ignition Flame safety system including burner interlocks, gas pressure sensing, flame sensing, automated N_2O/C_2H_2 ignition and shut-off Four-digit bipolar readout Readout in absorbance, concentration, or emission intensity Auto calibration Auto zero Peak reader Signal integration Curvature correction Flame emission standard

Options	Graphite furnace sampling system	$4,290
	A.A. microsampling system	650
	Flameless Mercury analysis system	550
	High sensitivity As/Se sampling system	425
	Auto 200 automated sampling system	3,500
	Deuterium Background Corrector	
	Printer sequencer	2,450
	Typewriter readout assembly	5,500
	Recorder	1,450
	Wavelength drive assembly	
References	Manufacturers Specifications	
Cost	Model 503, High Convenience Version	$15,000
Address	Perkin-Elmer Corporation Instrument Division Norwalk, CT 06856 (203) 762-1000	

Accessory Sample Furnace
Perkin-Elmer, Model HGA-2100



Class	Laboratory
Category	Air: Ambient, Source, or Vehicular Water: Fresh, Waste, or Saline Biomedical: Tissue, Urine, or Blood
Principle of Operation	Graphite Furnace: Sample is placed in a carbon tube, cup, or boat in a programmable furnace. Sample is dried, ashed, and atomized in an inert gas atmosphere.
Lower Detectable Limit	

Table I. HGA-2100 Detection Limits

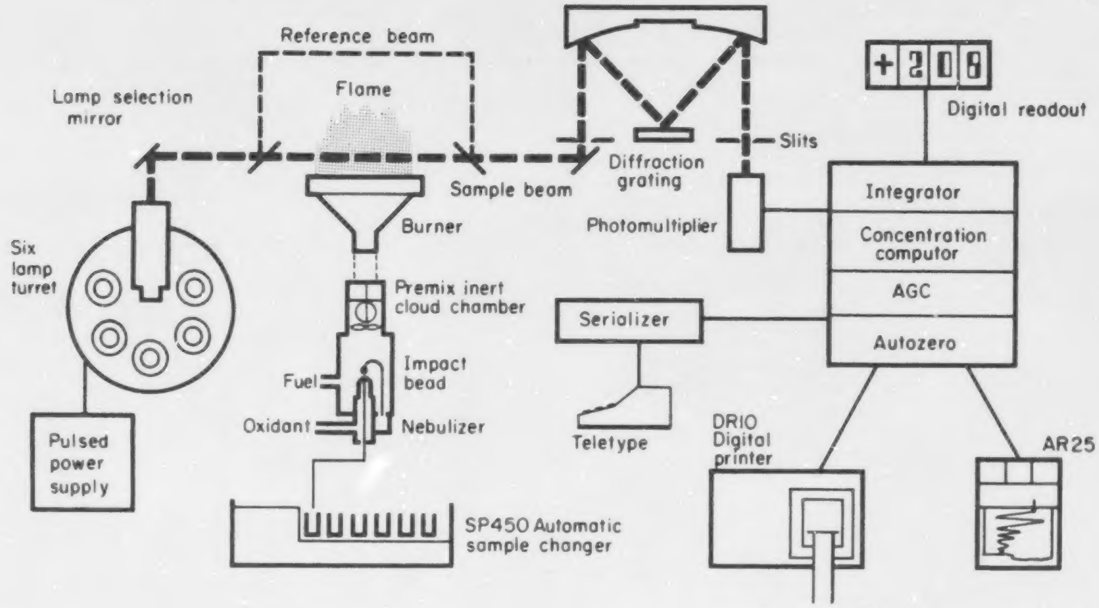
Element	Absolute (g x 10^{-12})	Relative (μg/l)*	Element	Absolute (g x 10^{-12})	Relative (μg/l)*
Ag	0.5	0.005	Li	30.	0.3
Al	5.	0.05	Mn	1.	0.01
As	10.	0.1	Mo	50.	0.5
Au	10.	0.1	Ni	100.	1.0
Ba	100.	1.0	Pb	5.	0.05
Be	3.	0.03	Sb	20.	0.2
Bi	10.	0.1	Se	50.	0.5
Cd	0.3	0.003	Si	80.	0.8
Co	40.	0.4	Sn	100.	1.0
Cr	10.	0.1	Te	10.	0.1
Cu	5.	0.05	Ti	2000.	20.
Fe	2.	0.02	V	500.	5.0
In	30.	0.3	Zn	0.1	0.001

**Based on a 100-μl sample volume.*

Range	From 10^{-13} grams, depending on element and wavelength
Interferences	Occasional problems from the formation of carbon compounds, from selective volatilization, and from background absorption. Matrix interferences can often be overcome by the method of additions.
Multiparameter Capability	68 single element lamps, 17 multielement lamps
Sampling	Method: Liquid or solid Volume: From < 1 to 100 µl
Performance	Accuracy: Dependent on accuracy of standards Reproducibility: 1-5% depending on sample and conditions Linearity: Better than 1% over optimum range Relative Humidity Range: Normal lab conditions
Operation	Calibration: Standard solutions Procedure: Direct injection of liquids or solids Unattended Period: None Maintenance: Minimal
Requirements	Power: 210-240 V, 15 amps, 50-60 Hz Weight: Power supply - 41 kg; furnace - 5.4 kg Dimensions: Power supply - 36 cm wide, 41 cm high, 56 cm deep Cooling Water: 1.5 liters/minute Inert Gas: Argon or nitrogen, 45 psig (3 kg/cm^2)
References	Manufacturer's Specifications
Cost	HGA 2100 $4,290
Address	Perkin-Elmer Instrument Division Norwalk, CT 06852 (203) 762-1000

Atomic Absorption Spectrophotometer

Pye Unicam, Model SP1900/SP1950


Reference beam
Flame
Lamp selection mirror
Sample beam
Diffraction grating
Slits
+ 2 0 8
Digital readout
Six lamp turret
Burner
Photomultiplier
Integrator
Concentration computor
AGC
Autozero
Premix inert cloud chamber
Serializer
Impact bead
Fuel
Oxidant
Nebulizer
Teletype
DRIO Digital printer
AR25
Pulsed power supply
SP450 Automatic sample changer

Class	Laboratory
Category	Air: Ambient, Source, or Vehicular Water: Fresh, Waste, or Saline Biomedical: Tissue, Urine, or Blood
Principle of Operation	Atomic Absorption Spectrophotometer: Double-beam, auto-zero, integration, auto-ignition, six position lamp turret, four digit display of concentration.

Lower Detectable Limit

Element		Wavelength nm	Flame type	Sensitivity µg/ml	Detection limit µg/ml	Precision %
Aluminium	Al	309·3	Nitrous oxide/acetylene	0·34	0·04	0·26
Arsenic	As	193·7	Air/acetylene	0·3	0·5	
Arsenic	As	193·7	Argon/hydrogen	0·22	0·1	
Barium	Ba	553·5	Nitrous oxide/acetylene	0·16	0·02	
Cadmium	Cd	228·8	Air/acetylene	0·009	0·002	
Calcium	Ca	422·7	Air/acetylene	0·05	0·0015	0·3
Calcium	Ca	422·7	Nitrous oxide/acetylene	0·017		
Cobalt	Co	240·7	Air/acetylene	0·035	0·0035	
Copper	Cu	324·8	Air/acetylene	0·026	0·002	0·12
Chromium	Cr	357·9	Air/acetylene	0·04	0·0035	
Gold	Au	242·8	Air/acetylene	0·08	0·015	0·18
Iron	Fe	248·3	Air/acetylene	0·049	0·006	
Lead	Pb	217·0	Air/acetylene	0·09	0·02	
Magnesium	Mg	285·2	Air/acetylene	0·0024	0·0001	
Manganese	Mn	279·5	Air/acetylene	0·021	0·0015	0·28
Molybdenum	Mo	313·3	Nitrous oxide/acetylene	0·18	0·025	0·45
Nickel	Ni	232·0	Air/acetylene	0·038	0·006	
Niobium	Nb	405·9	Nitrous oxide/acetylene	25	2·1	1·1
Potassium	K	766·5	Air/acetylene	0·017	0·0015	
Selenium	Se	196·0	Air/acetylene	0·26	0·35	
Silicon	Si	251·6	Nitrous oxide/acetylene	0·88	0·15	0·2
Silver	Ag	328·1	Air/acetylene	0·018	0·002	0·21
Sodium	Na	589·0	Air/acetylene	0·007	0·0008	
Strontium	Sr	460·7	Nitrous oxide/acetylene	0·042	0·002	0·38
Titanium	Ti	364·3	Nitrous oxide/acetylene	1·2	0·07	0·24
Zinc	Zn	213·9	Air/acetylene	0·009	0·002	

Range   ppb to % for 22 elements

Interferences

Multiparameter Capability   24 elements

Sampling   Method: Batch or automatic, flow spoiler, adjustable burner
Volume: 3.5 to 4.5 ml/min
Capacity: 50 samples with changer

Performance   Electronics: Solid state, printed circuit boards, monitoring taps .

Linearity:
Zero Stability: 0.003A per hour in AA mode
Scale Expansion: 0.1x to 20x
Damping: 1, 4, and 20 sec recorder time constant
Detector: Photomultiplier, S20 response
Range: 0 to 1.999 absorbance
Integration Time: 0.2, 1, 4, and 20 sec
10 signals per sec averaged

Monochromator: Ebert type

Grating: mm by mm
1800 lines/mm
Wavelength Range: 190 to 852 nm
Resolution: Limiting resolution 0.1 mm
Spectral Bandwidth: 2.2 nm per mm slitwidth at 200 nm
Drift: Less than 0.01 nm per °C

Gas Control: Separate fuel and oxidant flow meters, rotary control valves, electric ignition, safety interlock system.

Oxidant: Air or N_2O
Fuel: Acetylene
Venting:

Operation

Calibration:
Procedure: Instrument manual provided
Maintenance:
Training Required: Moderate

Requirements

Power: 100-120 V or 200-240 V, 50 or 60 Hz, 150 VA
Weight: 100 kg (220 lb)
Dimensions: 120 cm L, 61 cm H, 48 cm D (40", 24", 19")

Features

Model SP1950 has single lamp, no turret.

Options: Digital Printer	$2,200
Auto Sample Changer	2,195

References

Manufacturer's Specifications

Cost

Model SP1900	$11,950
Model SP1950	9,950

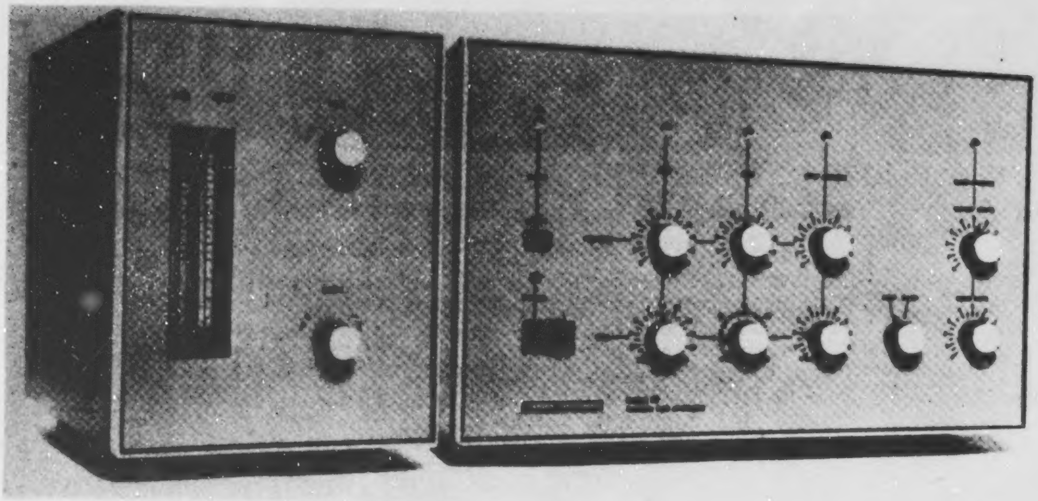
Address

Pye Unicam
750 S. Fulton
Mt. Vernon, NY 10550
(914) 664-4500

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

H2O-MET
Atomic Spectrometry
Varian Techtron 1A
Sept. 1975

Accessory Graphite Furnace
Accessory, Varian Techtron Model 63



Class Laboratory

Category

Air: Ambient, Source, or Vehicular
Water: Fresh, Waste, or Saline
Biomedical: Tissue, Urine, or Blood

Principle of Operation

Graphite Furnace: Sample is placed in a carbon tube or cup in a programmable furnace. Sample is dried, ashed and atomized in an inert gas atomsphere.

Lower Detectable Limit

Element	Absolute Grams	Concentration ng/ml in 5 µl sample	Element	Absolute Grams	Concentration ng/ml in 5 µl sample
Ag	2×10^{-13}	0.04	Li	5×10^{-12}	1.0
Al	3×10^{-11}	6.0	Mg	6×10^{-14}	.012
As	1×10^{-10}	20	Mn	5×10^{-13}	0.1
Au	1×10^{-11}	2.0	Mo	4×10^{-11}	8.0
Be	9×10^{-13}	0.18	Na	1×10^{-13}	0.02
Bi	7×10^{-12}	1.4	Ni	1×10^{-11}	2.0
Ca	3×10^{-13}	0.06	Pb	5×10^{-12}	1.0
Cd	1×10^{-13}	0.02	Pd	2×10^{-10}	40
Co	6×10^{-12}	1.2	Pt	2×10^{-10}	40
Cr	5×10^{-12}	1.0	Rb	6×10^{-12}	1.2
Cs	2×10^{-11}	4.0	Sb	3×10^{-11}	6.0
Cu	7×10^{-12}	1.4	Se	1×10^{-10}	20
Eu	1×10^{-10}	20	Sn	6×10^{-11}	12
Fe	3×10^{-12}	0.6	Sr	5×10^{-12}	1.0
Ga	2×10^{-11}	0.4	Tl	3×10^{-12}	0.6
Hg	1×10^{-10}	20	V	1×10^{-10}	20
K	9×10^{-13}	0.18	Zn	8×10^{-14}	0.016

Range 0.01 ppb to %

Interferences minimal, non-atomic absorption

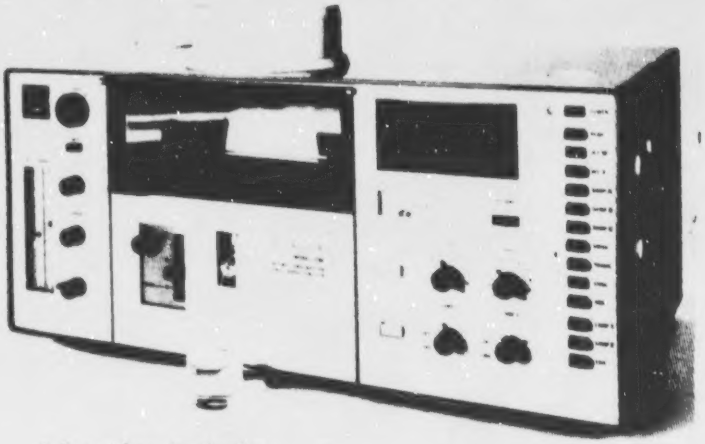
Sampling

Method: Liquid or solid
Volume: Up to 20 µl
Maximum Temperature: 3000°C
Atomizer configurations: 2 - cup or tube

Performance	Accuracy: ±1% to ±5% Reproducibility: ±1% to ±5%
Operation	Ambient Temperature Range: ambient - 3000°C Calibration: standard curve, method of standard additions Training: available upon request Unattended Period: 2 min. between samples Maintenance: minimal
Requirements	Power: 110/115 V, 220/240 V, 50/60 Hz Weight: 100 lb shipping weight Dimensions: (23" x 10" x 10")
References	Manufacturer's Specifications, Model 63 brochure
Cost	Model #63 $4,300
Address	Varian Techtron Varian Instrument Division 611 Hansen Way - D-425 Palo Alto, California 94303 (415) 493-8100 X3201

Atomic Absorption Spectrophotometer

Varian Models 1100/1200



Class	Laboratory Analysis
Category	Air: Ambient, Source, Vehicular Water: Fresh, Waste, or Saline Biomedical: Tissue, Urine, or Blood
Principle of Operation	Atomic Absorption Spectrophotometer: Sample is heated in a flame or carbon rod atomizer producing ground state atoms. The atoms then absorb resonant radiation emitted from a lamp source containing the element of interest. The absorption of the resonant radiation by the atoms is measured. The absorption is directly proportional to the atom concentration in the sample. The atom concentration in the sample can be determined by comparing the sample absorption with prepared standards run in a similar fashion.
Lower Detectable Limit	Depends on element, matrix and pre-concentration procedure method.

Element		Sensitivity µg/ml	Detection limit µg/ml
Ag	Silver	0.032	0.002
Al	Aluminium	0.75	0.018
As	Arsenic	0.64	0.44 0.15 0.002
Au	Gold	0.13	0.009
B	Boron	9.4	2.1
Ba	Barium	0.33	0.03
Be	Beryllium	0.016	0.002
Bi	Bismuth	0.33	0.11
Ca	Calcium	0.029	0.002
Cd	Cadmium	0.016	0.001
Co	Cobalt	0.075	0.012
Cr	Chromium	0.055	0.005
Cs	Cesium	0.16	0.014 0.01
Cu	Copper	0.040	0.002
Dy	Dysprosium	0.82	0.08
Er	Erbium	0.46	0.06
Eu	Europium	0.48	0.03
Fe	Iron	0.063	0.006
Ga	Gallium	0.72	0.061
Gd	Gadolinium	24	1.1
Ge	Germanium	1.3	0.11
Hf	Hafnium	13	1.4
Hg	Mercury	2.8	0.42
Ho	Holmium	0.76	0.035
In	Indium	0.42	0.060
Ir	Iridium	3.0	0.48
K	Potassium	0.01	0.005
La	Lanthanum	57	2.1
Li	Lithium	0.022	0.002
Lu	Lutetium	10	0.3
Mg	Magnesium	0.004	0.0002
Mn	Manganese	0.035	0.003
Mo	Molybdenum	0.28	0.03

Element		Sensitivity µg/ml	Detection limit µg/ml
Na	Sodium	0.007	0.0007
Nb	Niobium	29	2.6
Nd	Neodymium	6.3	1.7
Ni	Nickel	0.073	0.02
Os	Osmium	1.3	0.25
Pb	Lead	0.11	0.015
Pd	Palladium	0.11	0.016
Pr	Praseodymium	50	8.3
Pt	Platinum	1.5	0.09
Rb	Rubidium	0.035	0.004 0.0007
Re	Rhenium	10	1.1
Rh	Rhodium	0.15	0.006
Ru	Ruthenium	1.0	0.10
Sb	Antimony	0.47	0.074
Sc	Scandium	0.27	0.025
Se	Selenium	0.60	0.39 0.10 0.002
Si	Silicon	1.5	0.24
Sm	Samarium	6.6	0.75
Sn	Tin	0.61	0.03
Sr	Strontium	0.041	0.002
Ta	Tantalum	12	1.8
Tb	Terbium	9.2	0.78
Te	Tellurium	0.30	0.05
Ti	Titanium	1.5	0.05
Tl	Thallium	0.32	0.03
Tm	Thulium	0.27	0.014
U	Uranium	152	59.
V	Vanadium	0.75	0.05
W	Tungsten	9.7	0.95
Y	Yttrium	1.8	0.11
Yb	Ytterbium	0.073	0.002
Zn	Zinc	0.010	0.001
Zr	Zirconium	11	0.63

Range	ppb to % for some 67 elements
Interferences	Minimal for most analysis. Interference can be overcome by carefully selecting the proper flame conditions, and/or by adding chemical interference suppresants to the sample.
Multiparameter Capability	Can do 67 metals and metaloids directly and some molecular determination (i.e., Cl, SO_4, PO_4) indirectly.
Sampling	Method: Batch or automatic 4 samples/minute Capacity: 50 samples with sample changer
Performance	Electronics: Solid state incorporating a synchronous demodulated (lock-in) amplifier which pulses and detects the resonant radiation source at 285 Hz. System Stability: Better than ±0.5% tolerance for ±10% mains variation. Linearity: 0.5% of full scale deflection Scale Expansion: 0.3x to 50x Damping: 0.3, 1.5, 4.0 sec time constants Detector: Slide-on P.M. type R 446 Flame Emission: Emission chopper is built-in Monochromator: 0.25 meter Czerny-Turner with f/8 aperture ratio Grating: 32 x 27 mm 1276 lines per mm blazed at 275 nm Range: 185 to 900 nm Accuracy: ±0.2 nm Reproducibility: ±0.1 nm Stray light: Less than 0.1% at 200 nm Slit system: Step variable corresponding to 0.2, 0.5, 1.0 and 2.0 nm spectral bandwidth Gas Control: Separate fuel and oxident flow meters, rotary control valves, push button ignition, safety interlock system. Gas Combinations: Air/C_2H_2, N_2O/C_2H_2, Air/H_2, N_2/H_2 - entrained air, Air/propane, (N_2 and H_2 for CRA) Venting: Vent fan able to draw at least 200 cfm per instrument
Operation	Calibration: Procedure: Described in instrument and Analytical Methods Manuals provided Maintenance: All electronics are on plug-in circuit boards. The optics are generally maintenance free due to their simplicity. The monochromator is sealed. Training Required: Moderate, available on request
Requirements	Power: 110/115 V, 220/240 V, 50-60 Hz Weight: 27 kg (60 lb); 45 kg (98 lb) shipping weight Dimensions: 63 cm L, 35 cm H, 38 cm D (25", 14", 15")
Features	Output: Model 1100 - Meter (0 to 1.0 abs or 0 to 100% tolerance range) Model 1200 - Digital (0 to 9999 conc. units or 0 to 100% tolerance range) Options: Automatic Sample changer, Model 51 $1,375 Carbon Rod Atomizer, Model 63 4,300 Accessory Power Supply, Model 40 735 Hg,As/Se Kit, Model 64 490 Digital Printer for M1200, Model 36 2,615 Simultaneous background correction 1,400 Peak retrieval: An exclusive feature enabling the operator to use atomization techniques which generate quick response signals without a recorder. (i.e., CRA, cold-vapor Hg techniques, arsine generation techniques, etc.) Lamp turret: Four lamp turret
References	Manufacturer's bulletin

Cost	Model 1100	$5,990
	Model 1200	$6,550

HOLLOW CATHODE LAMPS

Element	Unit Price	Element	Unit Price
Aluminum	116	Molybdenum	121
Antimony	142	Neodymium	190
Arsenic	179	Nickel	121
Barium	151	Niobium	162
Beryllium	190	Osmium	277
Bismuth	150	Palladium	167
Boron	151	Platinum	190
Cadmium	156	Potassium	173
Calcium	121	Praseodymium	190
Cerium	185	Rhenium	190
Cesium	167	Rhodium	226
Chromium	121	Rubidium	167
Cobalt	121	Ruthenium	197
Copper	121	Samarium	190
Dysprosium	190	Scandium	249
Erbium	190	Selenium	160
Europium	249	Silicon	151
Gadolinium	190	Silver	128
Gallium	174	Sodium	167
Germanium	179	Strontium	167
Gold	179	Tantalum	156
Hafnium	197	Tellurium	167
Holmium	190	Terbium	179
Hydrogen Continuum	179	Thallium	151
Indium	162	Thulium	226
Iridium	202	Tin	156
Iron	121	Titanium	133
Lanthanum	190	Tungsten	133
Lead	144	Uranium	231
Lithium	151	Vanadium	190
Lutetium	226	Ytterbium	202
Magnesium	121	Yttrium	185
Manganese	128	Zinc	128
Mercury	144	Zirconium	156

MULTIELEMENT LAMPS

Sodium/Potassium	168.
Calcium/Magnesium	163.

Multielement Hollow Cathode Lamps are available, consisting of any combination of the following six elements: Iron (Fe), Cobalt (Co), Nickel (Ni), Manganese (Mn), Copper (Cu), and Chromium (Cr).

No. of Combinations	Unit Price
2	179
3	226
4	272
5	318
6	364

Remarks

Accessories available as modular attachments to the Model 1100/1200 are:

Hydrogen continuum lamp (used for background correction)	$ 179
Strip chart recorder 10" - Model A 25	$1,270
Standard solution of metals	$ 10-20/250 ml

The instrument is a single beam system with an optical design which enables it to operate through the UV-Visible range.

Address

Varian Techtron
Varian Instrument Division
611 Hansen Way - D-425
Palo Alto, CA 94303
(415) 493-8100 X3201

Atomic Absorption/Emission Spectrophotometer

Varian Techtron Model 1000

Class	Laboratory
Category	Air: Ambient, Source, Vehicular Water: Fresh, Waste, or Saline Biomedical: Tissue, Urine, or Blood
Principle of Operation	Single beam; automatic baseline correction; flame emission chopper; 10-cm meter readout; 4-lamp turret; pre-mix burner
Lower Detectable Limit	Depends on element -- usually ppb
Range	ppb to %
Interferences	Light scattering, non-atomic absorption
Multiparameter Capability	About 67 elements
Sampling	Method: Batch or automatic Volume: 4 xamples/minute (with flame)

Performance

Electronics:

Linearity: 0.5% of full scale division
Stability: Better than ±0.5% tolerance for ±10% mains variation
Scale Expansion: Continuously variable to 10×
Detector: R446 Photomultiplier
Zero Drift:
Span Drift:

Monochromator: Czerny-Turner mounting; 254 mm focal length

Grating: 32 × 27 mm, 1276 lines/mm
Wavelength Range: 186 to 900 nm
Spectral Bandpass: 0.2, 0.5, 1.0, 2.0 nm

Operation

Calibration: Standard solutions
Procedure: Calibration curve; standard additions, internal standard
Training: Available on request
Unattended Period: 20 min. with sample changer
Maintenance: minimal

Requirements

Power: 110, 115, 220, 240 Vac; 50 to 60 Hz;
Weight: 27 kg (59 lb)
Dimensions: 64 cm L × 35 cm H × 38 cm D (25" L × 14" H × 15" D)

Features

Output: Taut band meter, 10 cm mirror scale

Options:	
Automatic Sample Changer, Model 51	$1,375
Carbon Rod Atomizer, Model 63	4,300
Accessory Power Supply, Model 40	735
Hg,As/Se Kit, Model 64	490
Digital Printer, Model 36	2,615
Model 40 Lamp Power (for lamps 3 and 4)	735
Simultaneous background correction	1,400

References

(1) Manufacturer's Bulletin "Model 1000 Atomic Absorption Spectrophotometer," 11/72.
(2) Manufacturer's Price List, January 1, 1974.

Cost	
Model 1000	$4,790

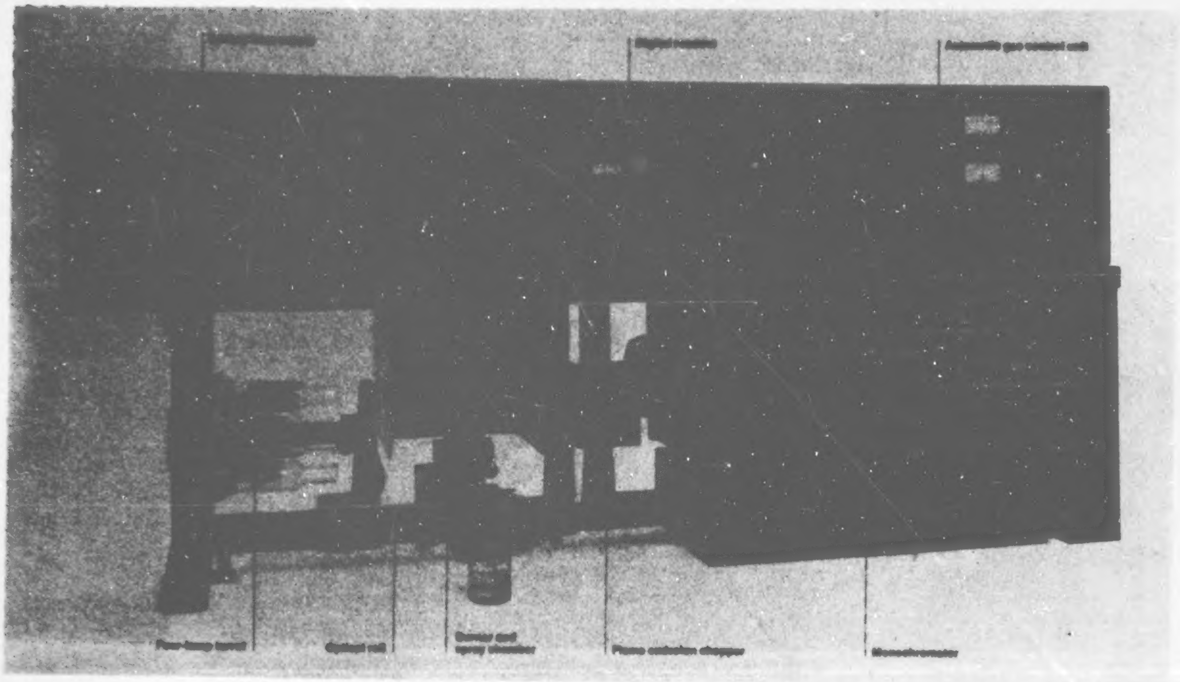
Remarks

Address

Varian Techtron
Varian Instrument Division
611 Hansen Way - D-425
Palo Alto, CA 94303
(415) 493-8100 X3201

Atomic Absorption/Emission Spectrophotometer

Varian Techtron Model AA-6



Class	Laboratory
Category	Air: Ambient, Source, Vehicular Water: Fresh, Waste, or Saline Biomedical: Tissue, Urine, or Blood
Principle of Operation	Single beam; 17 cm meter or digital readout; integration of signal output (3, 10 or 30 second integration periods); automatic calibration in concentration mode; scale expansion display; peak signal readout; auto zero; curve correction; automatic gas control unit; premix burner
Lower Detectable Limit	Depends on element -- usually ppb
Range	ppb to %
Interferences	Light scattering, non-atomic absorption some chemical interferences
Multiparameter Capability	About 67 elements
Sampling	Method: Batch or automated Volume: 4 samples/minute

Performance

Electronics:

Linearity: ±1% of full scale division
Stability: Better than ±0.5% of transmission for ±10% mains variation
Scale Expansion: 0.3 to 50×
Detector: R-446 photomultiplier
Zero Drift: Automatic zero

Monochromator: 0.5 m Ebert mounting

Grating: 50 × 50 mm, 638 lines per mm
Wavelength Range: 185 to 1000 nm
Resolution: 638 lines per mm
Dispersion: 3.3 nm/mm
Spectral Bandpass: 0.03 nm to 1.0 nm continuous

Operation

Calibration: Standard solutions
Procedure: Calibration curve; standard addition; internal standard
Training: Available on request
Unattended Period: 20 min. with sample changer
Maintenance: minimal

Requirements

Power: 110/115, 220/240 Vac; 50 to 60 Hz
Weight: 105 kg (230 lb)
Dimensions: 137 cm L × 62 cm H × 28 cm D (55" L × 25" H × 13-1/2" D)

Features

Output: Meter, digital, recorder, peak signal, digital printer

Options:	
Automatic Sample Changer, Model 51	$1,375
Carbon Rod Atomizer, Model 63	4,300
Hg,As/Se Kit, Model 64	490
Digital Printer, Model 36	2,615
Hydrogen continuum lamp (used for background correction)	179
Strip chart recorder 10" - Model A 25	1,270
Standard solution of metals	10-20/250 ml
Simultaneous background correction	1,400

References

(1) Manufacturer's bulletin "Model AA-6 Atomic Absorption Spectrophotometer," 1/73.
(2) Manufacturer's price list, January 1974

Cost

AA-6 $11,000 to $14,000

Address

Varian Techtron
Varian Instrument Division
611 Hansen Way - D-425
Palo Alto, CA 94303
(415) 493-8100 X 3201

C.2. CONTENTS FOR
ULTRAVIOLET AND VISIBLE ABSORPTION INSTRUMENTATION

1. Introduction
    a. Visual Photometers
    b. Filter Photometers
    c. Ultraviolet and Visible Spectrophotometers
        1. Radiation Sources
        2. Prisms
        3. Gratings
        4. Detectors
        5. Output
    d. Absorption Mechanisms
2. Applications
3. Instrument Comparisons
4. Summary and Recommendations
5. References
6. Table of Ultraviolet and Visible Absorption Instrumentation
7. Instrument Notes

Mnemonic

H2O-MET
UV-Visible

ULTRAVIOLET AND VISIBLE ABSORPTION INSTRUMENTATION

1. INTRODUCTION

Instruments which aid in chemical analysis by measuring the amount of ultraviolet and visible light absorbed by various compounds are discussed in this section. The basic objective of these instruments is to provide a quantitative measurement of the concentration of the compound or molecule of interest. The principal is to compare the light absorbed by a known calibrated sample with an unknown environmental or biomedical sample. Variations in the amount of light absorbed are related to the concentration of the unknown and form the basis for the measurement.

To maximize the usefullness of ultraviolet and visible absorption instrumentation, the user must (1) verify that the desired species has been formed, (2) choose a solvent which best enhances absorption by the species, (3) determine the best wavelengths to use in relating absorption intensity to concentration, (4) become aware of interferences, (5) evaluate reproducibility and recognize variables in the procedure.

Environmental sample analysis techniques discussed in this section may be divided into three categories: (a) visual photometers, (b) filter photometers, and (c) spectrophotometers.

a. Visual Photometers

Visual photometers use a human eye as the detector and a brain as the discriminator. Unfortunately, the eye has a very limited spectral range, low accuracy in distinguishing intensities, high fatigue rate, and slow response in comparison to other techniques. Hence, visual detection is severely limited to a relatively few determinations in which low accuracy is sufficient.

In order to make colorimetric comparisons, white light is usually used and the condition of equal transmission of light by the standard and the sample is determined in either of two ways: (1) the observer relies upon his judgment of color intensity or hues; (2) a photoelectric cell replaces the eye of the observer and judgment is made by virtue of a meter reading. Visual colorimetry usually involves the use of flat bottomed tubes and often daylight reflected from a white surface is used for illumination. The concentration of the unknown may be determined by comparison with a series of known standards and choosing the best match. Alternatively, a single concentrated standard may be used which is diluted by known amounts until a match is obtained with the unknown.

Visual comparisons are also made using a Duboscq comparator of the type diagrammed in Figure 1. The instrument allows a standard and an unknown solution to be penetrated to different amounts by glass rods, through which observations are made. The farther the penetration of the glass rod, the shorter the effective length of the colored solution; by equalizing the intensity of color, the concentration of the unknown can be determined (Ref. 1).

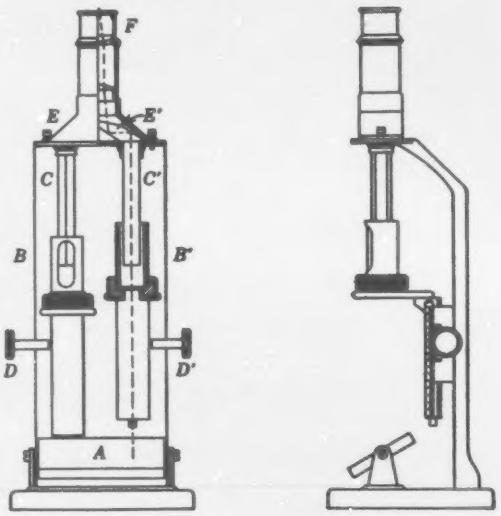


Figure 1: Schematic diagram of Duboscq comparator (Ref. 1, Mellon p. 156).

The sensitivity for detection of a colored substance can be defined as the smallest weight that can be detected in a column of solution of unit cross section. Sandell (Ref. 2) has compiled a list of sensitivities for the visual perception of a variety of substances. These sensitivities range from 0.01 to 10 μgm/cm^2 depending upon the substance. In general an observer can distinguish between two solutions which differ in concentration by 7%.

b. Filter Photometry

Filter photometers may be either single or double beam instruments. Optical filters are used to separate the wavelengths of interest; no grating or prism monochromators are used. Combinations of different filters can be used to select various wavelength regions; however, the bandpass of these instruments is rather broad and may not allow sufficient wavelength selectivity depending on the analysis. Another drawback to this instrumentation is its inability to perform adequately in the ultraviolet region.

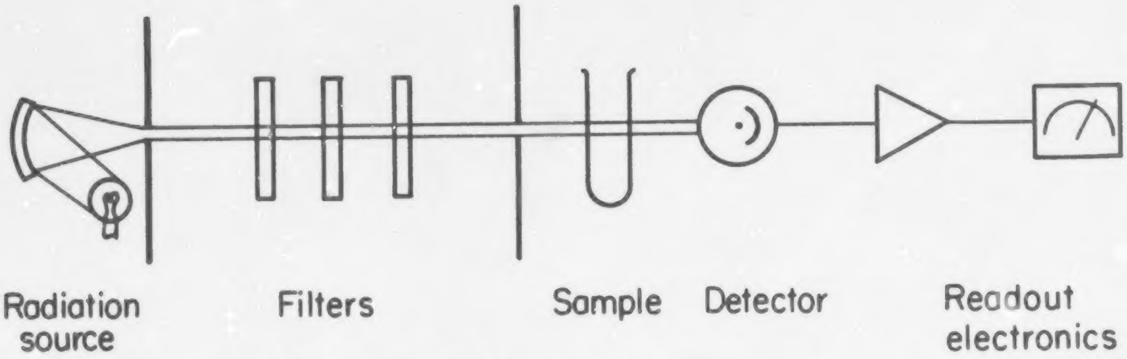


Figure 2: Components of a single beam photoelectric filter photometer.

Preconcentration steps and chemical separation procedures would aid the selectivity for this as well as other techniques. The filters pass enough energy such that moderately sensitive detectors, such as phototubes, may be used. Since the cost is moderate, filter photometers have been used in continuous-monitoring and low accuracy routine analysis.

Single beam instruments as outlined in Figure 2 consist of a radiation source, light filters, sample space, phototube detector, and readout electronics. Double beam instruments may be optically or electrically balanced. Intensity of the radiant energy in the optically compensated design is decreased by a diaphragm until it matches the intensity of radiation passing through the unknown. A detector having a nonlinear response to intensity may be used. Electrically compensated double beam versions use photentiometers to balance the outputs for blank samples. The ratio between unknown and calibration samples may then be recorded. Filter photometers can fill a need for inexpensive "ballpark" instruments.

c. Ultraviolet and Visible Spectrophotometers

Ultraviolet and visible spectrophotometers are comprised of (1) a radiation source, (2) grating or prism monochromator, (3) sample compartment, (4) detector, and (5) display electronics, as diagrammed in Figure 3. The radiation source may be a tungsten lamp or a deuterium or a hydrogen discharge lamp. The monochromator may be a Czerny-Turner, Littrow, or Ebert mount using a grating or a prism. The sample compartment may be temperature controlled or automated for special purpose applications. Phototubes, more sensitive photomultiplier tubes, or solid state crystals may be used as detectors. The display electronics may include graphical recorders, analog meters, or digital displays.

Instrumental spectrophotometric methods have several advantages: the selectivity may be increased by restricting measurement to the spectral region of maximum absorption, hence

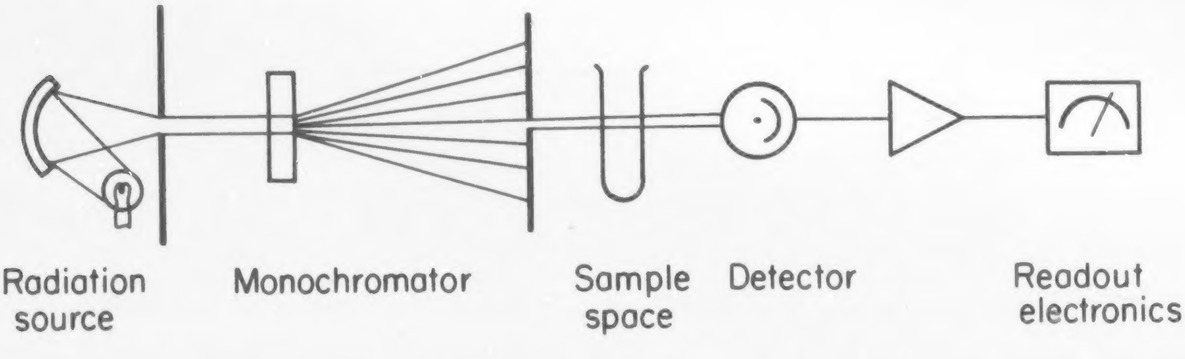


Figure 3: Components of a molecular absorption spectrophotometer (Ref. 7).

the effects of interfering substances which absorb at nearby wavelengths may be reduced; higher accuracy, precision and sensitivity can be obtained with electronic photodetectors than with an eye, and if large numbers of samples are involved, effects due to eye fatigue are eliminated.

1. Radiation Sources

Radiation sources should be selected based on the uniformity of intensity over the wavelength range of interest. The radiation source should provide sufficient energy within the wavelengths being examined; however, radiation sources are not considered a problem for routine analysis. Long term stability, quality control in mass production, and lifetime are the current considerations rather than a basic need for new lamps. A variety of lamps including xenon, deuterium, mercury, and tungsten are available. These lamps emit electromagnetic radiation over a rather broad spectrum, as compared to hollow cathode lamps used in atomic spectroscopy.

Anything that can be done to increase the intensity in the ultraviolet is highly desirable. Most instruments lose transmission in this region because of the characteristics of the wavelength isolation device, the absorption of the optical elements and the response of the photodetector. The substitution of deuterium for hydrogen as a source of ultraviolet radiation has been of some help. The use of quartz iodide tungsten lamps has provided more intensity in the visible and near ultraviolet region. A tungsten filament lamp covers the visible region down to about 340 nm in the ultraviolet. The continuum from a hydrogen discharge lamp is used in the ultraviolet (350-200 nm).

2. Prisms

A monochromator is used to separate the wavelength of interest. A wide variety of monochromators are available using either prisms or gratings to select the desired wavelength. Prisms have a high optical efficiency but are somewhat temperature sensitive. Quartz is used as a prism material primarily due to its wide wavelength bandpass. Calcium fluoride, sodium chloride, and potassium bromide are also used as prism materials for special purpose work, primarily in the infrared region. However, calcium fluoride has a limited range, sodium chloride is somewhat difficult to clean, and potassium bromide is hydroscopic which requires a dry atmosphere. Prism instruments are being replaced by grating instruments due to a more linear dispersion factor, higher resolution, improved versatility, and competitive cost.

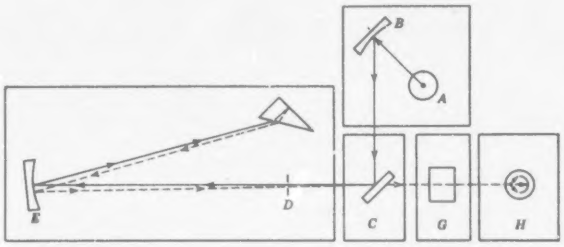


Figure 4: Schematic optical diagram of the Beckman DU spectrophotometer (Ref. 3, p. 3010).

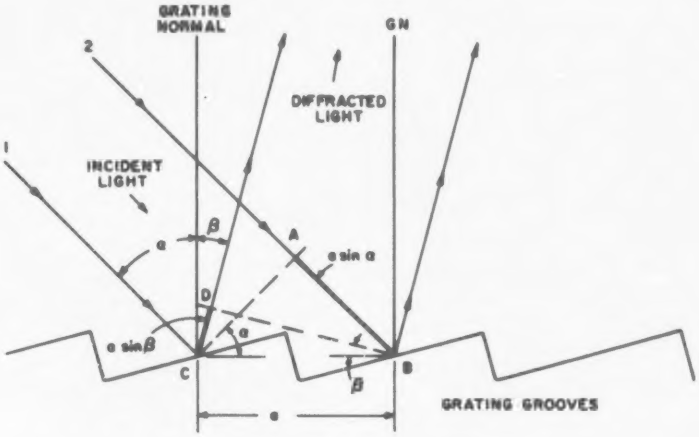


Figure 5: Diagram to show phase relation between rays diffracted from two adjacent grating grooves. (Ref. 4).

A typical optical system for a prism instrument is shown in Figure 4. The Beckman DU Spectrophotometer is a single beam instrument which uses a quartz Littrow prism and a single slit. Light source A (hydrogen lamp for ultraviolet or tungsten for visible) emits light which is reflected and focused by mirror B. Half silvered mirror C reflects light which is collimated by slit D. Mirror E reflects the selected light beam to the prism which refracts the beam to spread out the various wavelengths. The wavelength of interest is chosen by rotating the prism and the reflected beam (dotted) is sent back through slit D and mirror C. The monochromatic light then passes through the sample space G to the detector H. The detector may be a "blue" or "red" sensitive phototube which converts the signal to an electrical pulse which is amplified and drives a meter. The amount of monochromatic light absorbed by the sample is proportional to the concentration of the material in the sample being studied.

3. Gratings

Many of the new instruments that are being developed and manufactured today include a grating monochromator. A brief history of gratings is described in Reference 4, beginning in 1785 with David Rittenhouse. The process and machinery for manufacturing grating masters and replicas is also discussed. The following is taken from Reference 4 and describes the basic principles of diffraction gratings and dispersion.

> "When light is incident on a grating surface it is diffracted from the grooves. In effect, each grating groove becomes a very small, slit-shaped source of reflected or transmitted light. The usefulness of a grating depends on the fact that there exists a unique series of angles where, for a given groove spacing and wavelength, the light from all the facets is in phase. This can be visualized from the geometry of Fig. 5, which shows a plane wavefront, incident at an angle α, with respect to the grating normal, and diffracted at an angle β. The principle of interference dictates that only when this difference equals the wavelength of light, or a simple integral multiple thereof, will the light from successive grooves be in phase, i.e., reinforce itself. At all other angles there will be destructive interference between the wavelets originating at the groove facets.

"These relationships are expressed by equation (1) below, known as the grating equation, since it governs the diffraction behavior of all gratings:

$$m\lambda = a(\sin \alpha \pm \sin \beta) \qquad (1)$$

where α = angle of incident rays with respect to a normal to grating.
β = angle of diffraction with respect to normal. The plus sign signifies that β is on the same side of the normal as α while the minus sign signifies that β is on the opposide side of the normal.
a = grating constant or distance between successive grooves.
m = the diffracted order, usually a small integer.
λ = diffracted wavelength.

"It is evident from this equation that for a given order and grating spacing there is a purely mathematical (sine) relationship between wavelength and the angles of the incident and diffracted rays. Both rays are assumed to be in a plane perpendicular to the rulings. When m is zero, the grating acts as a mirror, all wavelengths being superposed.

"In the special but common case, when $\alpha = \beta$ (Littrow configuration), the grating equation simplified to

$$m\lambda = 2a \sin \beta \qquad (2)$$

DISPERSION

"The angular separation $d\beta$ of two different wavelengths of light differing by $d\lambda$ can be obtained by differentiating the grating equation (1), assuming the angle of incidence α to be fixed:

$$m d\lambda = a \cos \beta d\beta \qquad (3)$$

$$\text{or } \frac{d\beta}{d\lambda} = \frac{m}{a \cos \beta} = (m/a) \sec \beta \qquad (4)$$

"The ratio $d\beta/d\lambda$ is known as angular dispersion. The linear dispersion of a grating system is the product of this and the effective focal length. The usual instrument design calls for as much linear dispersion as possible in an instrument whose compactness limits focal length. Hence the desire for relatively large angular dispersion."

The preferred wavelength dispersion element is a grating. The bandpass produced by gratings is more narrow than prisms for most regions of the spectrum and is essentially constant throughout the ultraviolet and visible region. They can be so constructed that most of the intensity falls in a specified wavelength region. One main limitation is stray light in the ultraviolet. Recent developments in the production of holographic gratings will lessen this problem.

A double grating monochromator having two gratings in optical series in shown in Fig. 6. This arrangement allows one to increase the wavelength resolution and dispersion. Another spectrophotometer having two gratings is shown in Fig. 7 (Ref. 5). The optical system has two monochromators; however, in the splitbeam mode only one is used. The emerging light is chopped into a sample and reference beam. The photomultiplier (PMT) is quite close (3 mm) to the sample to enhance the measurement of turbid samples.

A wide variety of monochromator configurations are commercially available with each manufacturer's product being somewhat different. In general, the wavelength accuracy, precision, and resolution specified by the manufacturers describe the performance of the entire instrument including the light source, monochromator, and detector.

4. Detectors

Various types of photoemissive devices are utilized as detectors: the vacuum phototube, the gas phototube, and the photomultiplier. All of these tubes depend upon the emission of electrons when photons strike a photosensitive surface as their principle of operation. The gas phototube may yield an

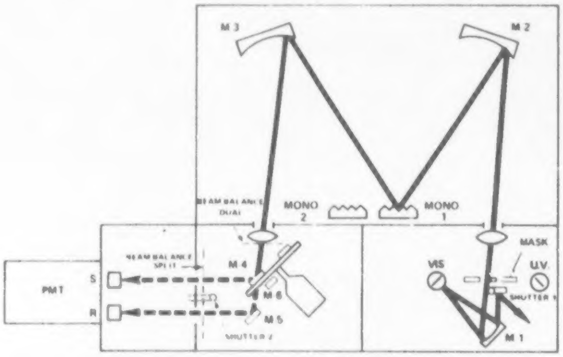


Figure 7: Optical diagram, split beam mode, American Instrument Company (Ref. 5).

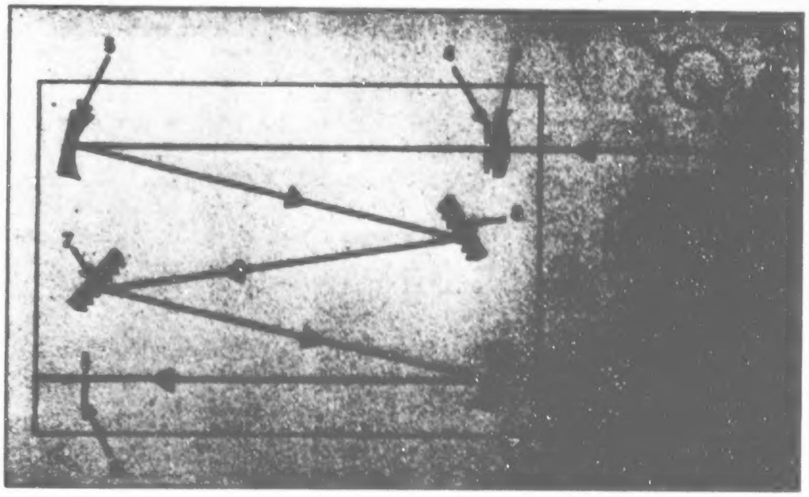


Figure 6: Bausch & Lomb "Grating Monochromator". The beam from a light source (1 or 1A) depending on the rotation of the condensing mirror (2) is focused on the entrance slit (4) by the slit collective lens (3). The beam then passes through to the collimating mirror (5) and is reflected to the first reflectance grating (6), where it is dispersed, then to a second reflectance grating (7), where it is further dispersed. The twice dispersed beam is reflected from the second collimating mirror (8) and passes through the exit slit (9).

Table 1
Photometric Detectors (Ref. 3, p. 2999).

	Barrier Cell	Vacuum phototube	Gas phototube	Photo-multiplier
Effect	Photovoltaic	Photoemissive	Photoemissive	Photoemissive
Sensing element	Junction of semiconductor on metal	Alkali metal oxide coating	Alkali metal oxide coating	Alkali metal oxide coating
Frequency range, nm	400-800	200-1000	200-1000	160-700
Type of output	High current or e.m.f.	High current	High current	Very high current
Sensitivity	Moderate, frequency-dependent	High, frequency-dependent	Frequency-dependent	Very high
Response time	Fast	Very fast, 11 sec	Moderately fast	Very fast

amplification of 5 to 10 times that of the vacuum tube since electrons which are accelerated from the photocathode cause ionization of gas atoms with a consequent increase in current. The photomultiplier causes the emitted electron to strike several electron emitting surfaces with acceleration between each encounter. This can result in amplification factors as great as 10^8, hence very low light levels (single photons) can be detected. A relative comparison of several photometric detectors is given in Table 1.

Tektronix recently introduced a spectrometer which uses a silicon vidicon as the detector. Photons which survive the optical path strike a silicon target (a modified Television camera detector) and accumulate a localized electron charge on the surface of the silicon. An electron beam scans the back side of the silicon in the same fashion as an ordinary TV raster scan and displays the information on an oscilloscope display. Since the scanning is performed electronically, greater speed can be obtained. (See Instrument Note)

5. Output

The presentation of the output may be achieved with a direct measurement design, with a null balance design or with an automatic recording operation. The direct measurement design uses a photovoltaic cell and the degree of reliability will depend on the quality of such components as the detector and the meter. The null balance design involves comparing the output signal with a reference signal and the reliability of the measurement depends upon the quality of the electronic balance circuit.

Recorders are often offered as an option, separate from the basic instrument. Some instruments have a built-in wavelength scanning feature to do spectral analysis. The recorders used in these instruments must be synchronized and have a wide dynamic range and accurate drive systems. The response may be linear (ask, how linear) or log (ask, within what percent).

Since a recorder and its associated synchronization electronics adds several thousand dollars to the cost of an instrument, it should only be considered for research work. Routine analysis of environmental or occupational samples do not require the sophisticated capabilities of scanning recording spectrophotometers. Limited funds are better spent on automatic sample handling equipment, and a digital printer. A printer having a high and low set point, and means for indicating measurements which exceed the pre-set limits (e.g., prints with red ink) are useful output devices for routine analysis. Recording the data in a permanent, accurate, and legally acceptable manner is the desired end result; an instrument and a procedure for its use which meets this goal should be selected.

d. Absorption Mechanisms

The description in this section will emphasize the mechanisms responsible for absorption of light by molecules in solution. It has been found that the intensity of light (I) transmitted through such solutions obeys the relationship

$$I = I_o 10^{-Ecd}$$

where I_o = intensity of incident light
E = molar absorptivity
c = concentration
d = thickness of absorbing material.

The molar absorptivity is a measure of the strength of the interaction between the incident light and the absorbing material and it is this quantity which will be discussed in greater detail.

According to classical physics the interaction of light with the absorbing molecule induces an electric dipole into the absorbing substance and molar absorptivity increases as does the out-of-phase polarizability of the absorber (Ref. 6). The corresponding quantum mechanical description pictures an electron in the molecule being raised from the ground state to some excited state by the interaction with light. In this case the value of the molar absorptivity depends upon the square of the value of an integral which involves the wavefunctions of the initial state, final state and the electric dipole moment between these states. An upper theoretical limit for the value of the molar absorptivity has been calculated. Upon the assumption that the half width of the absorption band is 2000 cm^{-1} this value is of the order of 10^5 cm^{-1}. This upper limit has been predicted by other arguments and is borne out experimentally. Aromatic compounds have molar absorptivities of this order in the ultraviolet whereas other compounds more commonly have smaller values.

Electron transitions between initial and final states can be categorized into four different types: (1) both states are localized on a single atom, (2) both states are localized on a portion of the atoms of a molecule, (3) both states are nonlocalized (i.e., penetrate the whole molecule), and (4) one state is associated with one molecule and the other state is associated with another molecule (charge-transfer transitions). The rare earth ions, the actinides, and the transition metals provide examples of transitions between levels which are localized on single atoms. When the electron transitions occur between levels localized on a group of atoms that group is referred to as a chromophore. Some of the more common chromophores with the location and strength of their transitions are listed in Table 2.

The first four chromophores in Table 2 illustrate the principle that the transition intensity of chromophores in a complex molecule tends to be additive. However, if the chromophores are separated by single bonds the states become nonlocalized in the sense that they extend over more than one bond. This causes the absorption band to extend over a larger wavelength and to become more intense. Substances such as dyes, pigments, vitamins, and hormones provide examples of transitions between non-localized states.

Table 2
Chromophoric Groups (Ref. 3, p. 2952)

Chromophore	$\lambda_{max.}$ (mμ)	log ε
C=C	190	3.5
$(C=C)_2$	220	4.2
$(C=C)_3$	260	4.6
$(C=C)_4$	290	4.8
-COOH	210	1.6
C≡C	180	<2
$-CONH_2$	210	2.2
C=N	190	3.7
C≡N	170	<2
C=O	280	1.3
C=S	330	1.0
N=N	370	1.2
N=O	660	1.3
$-NO_2$	270	1.2
-ON=O	370	1.7
$-ONO_3$	270	1.2
	Rings:	
Phenyl-	270	2.4
Pyridyl-	260	3.2
Naphthyl-	310	2.4
Cyclopentadiene	244	3.4
Pyrrole	240	2.4
Pyrimidine	245	3.5
Quinoline	310	3.8
Anthracene	380	2.8

Generalizations: (1) the absorptions of two chromophores are additive when joined by an aliphatic link; (2) two chromophores form a new chromophore if attached directly; (3) addition of a C=C link to a conjugated chain increases $\lambda_{max.}$ by ca. 30 mμ and log ε by ca. 0.3; and (4) replacement of C=C in a chromophore by C≡C does not greatly affect either $\lambda_{max.}$ or log ε.

Spectra of a large number of inorganic as well as organic complexes can best be interpreted in terms of an electron transition whereby there is a transfer of charge between the interacting species that comprise the complex. These types of transitions tend to be very intense and are particularly well suited for analytical purposes. $FeSCN^{2+}$, PbI^+, and $CuCl^+$ are examples of complexes that exhibit charge transfer in the visible or ultraviolet spectral region.

2. Applications

The object of ultraviolet and visible spectrophotometry is to form intensely colored compounds of the type described above, which involves the element to be determined in the formation process. The more intensely colored the compound, the more sensitive the analytical method. The desirable characteristics of color formation reactions are high sensitivity, specificity, good reproducibility, color stability, and adherence to Beer's Law. These desiderata are discussed at greater length by Sandell (Ref. 2). Detailed procedures for 45 different elements are also contained in this reference. A review article by Boltz and Mellon (Ref. 8) describes procedures which have been developed since Sandell's publication.

In a few cases (i.e., Al, Be, Ga, In, Sc, U, and Zr) fluorimetric methods are more sensitive and more selective than are colorimetric methods. The analysis consists of forming a fluorescent compound from the element of interest, exciting the fluorescence by radiation of a suitable wavelength (usually the ultraviolet), recording the emitted fluorescence usually at a longer wavelength, and relating the intensity of the fluorescence to the concentration of the element of interest by running a number of samples of known concentration. The dependence of the emitted intensity upon such factors as exciting intensity, concentration of emitting species, and instrumental design are discussed by Sandell (Ref. 2). A series of review articles have been published which discuss more recent advances in this field (Ref. 9).

Ultraviolet and visible spectrometry are used to determine a wide variety of materials in liquid samples. Concentrations of metals such as cadmium, lead, iron, and copper can be determined in liquid samples. If the sample is urine, saliva, or relatively clear mucous, the determination of the concentration of the unknown pollutant is straight forward. However, if the sample is turbid or more highly absorbing such as bone cells, then the measurement is more difficult.

Table 3 was compiled from Reference 10 and lists the wavelengths and light path required for various materials in drinking water.

Reliable data on the lower detectable limits for various specific elements and compounds is very difficult to obtain. Very few manufacturers specify in ppb the limitations of their instruments. For analysis of environmental and biomedical samples, one will need to measure the absolute concentrations of several pollutants dispersed in turbid samples. Although much information is derived from pure samples (rather than mixed), at least benchmark measurements can be specified. If long complex analytical procedures (recipes) are required to separate out the item of interest, then the opportunity for human error increases, although the specificity also increases.

Table 3
Wavelength and light path for various materials in drinking water samples (Ref. 10).

	λ wavelength (nm)	l, light path (cm)
Cadmium	515	1 cm
(Hexavalent) chromium	540	
(Total) chromium	540	1 cm or longer
Copper	457	1 cm or longer
Cyanide	620-630	1 cm
Iron	510	1 cm or longer
Lead	520	1 cm or longer
Manganese	525	1 cm or longer
Nickel	445	1 cm or longer
Phenols	460	1 to 10 cm
Potassium	425	1 cm or longer
Zinc	535	1 cm or longer

Determination of the minimum difference in absorbance (e.g., between a sample and a blank reference) could be specified. This would give the analyst a means for comparing the performance of competitive instruments.

3. Instrument Comparisons

Information has been accumulated which describes the characteristics of most of the spectrophotometers which are commercially available. An attempt was made to obtain information pertaining to the five basic building blocks of the instrument (radiation source, wavelength isolation, sample compartment, detection system, and output presentation). The quality of the combined light source and detection system can be inferred from the stability. The quality of the wavelength isolation can be inferred from the wavelength resolution. The instrument notes provide a starting point for the decision on which instrument best fits the need of a specific research or analytical effort.

As can be seen from the table which summarizes the characteristics of spectrophotometers, the price of these instruments ranges from about $400 to $27,000. There are many features which explain this large range in price. Automatic wavelength scanning increases the price since a method must be constructed of turning a prism or grating in a reproducible manner. In order to correct for variations of source intensity, transmission, and detector sensitivity, double beam operation is valuable. Some instruments allow a scale expansion so that either the range of from 0-1, 0-10, or 0-100% T can be recorded on chart paper. Extensive wavelength coverage can be somewhat expensive. In order to detect radiation at 185 nm, special quartz optics must be used; the photomultiplier tube must also be especially chosen, and the source ultraviolet intensity should be high. A totally different light source and detector will be required for the region higher than 800 nm.

4. Summary and Recommendations

Existing instrumentation is considered adequate for routine analysis of some materials in air, water, and biomedical samples. A list of the elements and compounds which can safely be analysed and the analytical procedures to be followed are given in References 8 and 10 for air and water samples. Due to variations in the matrix (each of which needs to be subtracted using a different procedure), there is no single "bible" for biomedical sample analysis. However, since many of the samples are liquids (e.g., urine), the water analysis procedures can be applied.

A side by side comparison using a wide range of calibrated samples should be performed by an independent research facility. Also an instrument/laboratory certification program is recommended to check the procedures, accuracy, and uniformity of the measurements. The National Bureau of Standards could perform this task. Given the sparse performance data that is available, it is very difficult to make an informed choice among the many instruments, even when specific routine analytical tasks have been defined.

One measure of an instrument's performance is to test the minimum difference in absorbance that can be detected at very low concentrations. After preparing one calibration sample, split it into several samples and dilute several of the sub-samples a very small amount. A complete demonstration of the instrument's performance using typical environmental, calibration, and blank samples should be requested before selecting a specific instrument.

Several improvements in the existing instrumentation are desired for research work using ultraviolet and visible absorption instrumentation. Improvements in differential absorptivity in the ultraviolet to be able to study turbid water samples are recommended.

The lower detectable limit of an instrument is the result of a combination of limitations including: the amount of light emitted by the lamp, the amount of light passed by the monochromator, the amount of light absorbed by the sample, and finally the sensitivity of the detector, all at the wavelength of interest. However, the major limitations are not a strong function of the optics, detector, and electronics. Sample preparation procedures and means for preparing a sample in a uniform, repeatable and efficient manner are more important limitations when attempting to analyze environmental samples.

Fluorescence UV-VIS spectrophotometry suffers from several interferences. First, the signals are small and hence the stray light becomes a limiting factor. Although detectors are available to sense extremely low levels of light, the low signal to noise ratio in fluorescence work is restrictive. Scattering and re-absorption of signals which emanate from the center of the sample volume will tend to provide a lower concentration reading, especially for turbid samples. The usual problems of sample uniformity, settling, temperature sensitivity, and pH sensitivity (phenols) add to the uncertainty of the usefulness of the measurements.

Problems associated with sample and data handling limit this technique, rather than a basic need for improved instruments. Other competing instrumental techniques (e.g., atomic spectrometry, neutron activation, x-ray fluorescence, etc.) need to be compared to absorption and fluorescense spectrophotometry with the proposed applications in mind. UV-VIS spectrophotometric instruments are widely available, are adequate for many routine analytical tasks, and have a high performance to price ratio.

5. References

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5. R.L. Sellers, G.W. Lowy, and R.W. Kane, "A Versatile UV-VIS Spectrophotometer," American Laboratory, March 1973.

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9. A. Weissler, "Fluorometric Analysis," Analytical Chemistry, Vol. 46, No. 5, p. 500R (April 1974).

10. Standard Methods for the Examination of Water and Wastewater, 13th Edition, American Public Health Association, Washington, DC 20036 (1971).

6. TABLE OF ULTRAVIOLET AND VISIBLE ABSORPTION INSTRUMENTATION

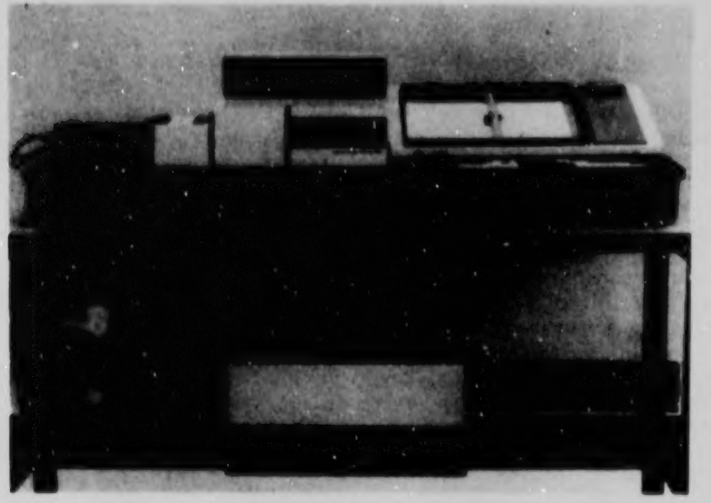
Instrument	Wavelength Range (nm)	Wavelength Accuracy (nm)	Wavelength Resolution (nm)	Cost	Remarks
American					
DW-2™	200-825	±0.2	< 0.3	$20,895.	Wavelength scanning
Baird Atomic					
FM-200		10		$ 890.	
FP-100	220-770	2	2	$ 5,874.	Fluorometer Automatic or manual scanning
SF-100	220-700	2	2	$ 8,600.	Spectrofluorometer 2-speed wavelength scanning
Bausch & Lomb					
Mini Spec ™ 20	400-700	±3	20.0	$ 495.	Portable, battery operated
Spectronic® 20	340-950	2.5	20.0	$ 525.	Regulated model, $595.
Spectronic® 70	325-925	1.0	8.0	$ 875.	
Spectronic® 88	"	"	"	$ 1,195.	Concentration
Spectronic® 100	"	"	"	$ 2,195.	Digital readout, concentration
Spectronic® 200	190-800	±0.5	0.25	$ 4,895.	Wavelength scanning
Spectronic® 210	190-900	"	"	$ 6,000.	Digital, wavelength scanning, Concentration
Spectronic® 700	200-950	1.0	2.0	$ 2,600.	Concentration
Spectronic® 710	200-1000	"	"	$ 3,000.	Digital, concentration
Beckman					
24	340-700	±0.5	4.0	$ 3,300.	Wavelength scanning
25	190-700	"	0.2	$ 5,300.	Wavelength scanning
26	"	"	"	$ 5,500.	"
ACTA CIII	"	+0.1	"	$ 9,910.	
ACTA M-IV	190-3000	±0.5 (UV-Vis) ±2.5 (NIR)	0.02 (UV-Vis) 1.2 (NIR)	$ 16,700.	
ACTA M-VI	"	±0.1	< 0.05	$ 15,800.	

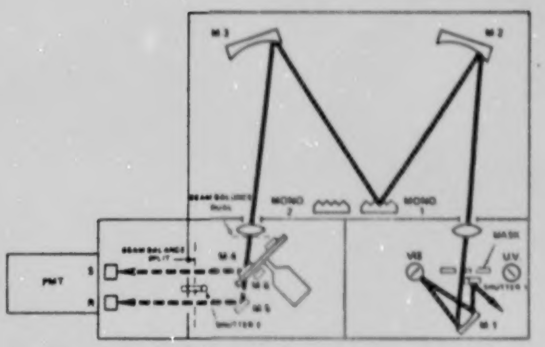
(Continued)

Instrument	Wavelength Range (nm)	Wavelength Accuracy (nm)	Wavelength Resolution (nm)	Cost	Remarks
Varian					
Cary 118C	185-800		0.02 @ 200 nm 0.1 @ 350 nm	$17,250.	Ratio recording/scanning
635 M	190-900	>±0.5	0.2	$ 5,300.	
635 D	"	"	"	$ 6,400.	
Carl Zeiss					
PM2 D	200-1,000	1	10	$ 2,485.	
PMQ 3	185-2,500	<0.05 @ 200 nm	0.03 (UV) 1.0 @ 600 nm	$ 7,984.	

Ultraviolet/Visible Spectrophotometer

American Instrument, DW-2™




M 3
M 2
BEAM BALANCE DUAL
MONO 2
MONO 1
BEAM BALANCE SPLIT
M 4
PMT
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M 5
SHUTTER 2
MASK
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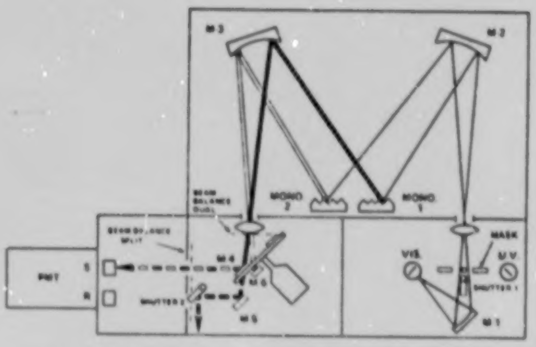
M 1

Figure 1 *Optical diagram, split-beam mode.*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SHUTTER 1
M 1

Figure 4 *Optical diagram—dual wavelength, dual-wavelength scanning, derivative and kinetic modes.*

Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Single beam, split beam, dual wavelength, dual wavelength-scanning, derivative, and kinetics modes
Lower Detectable Limit	

Range

Absorbance: 2.0, 1.0, 0.5, 0.2, 0.1, 0.05, 0.02, 0.01, 0.005 full scale
Transmittance: 100%, 50%, 25%, 10%, 5%, 2.5%, 1% full scale

Interferences

Multiparameter Capability

Sampling

Method: Batch
Volume: 3 ml standard, other with accessories
Temperature control connections; removable quartz diffuser plate

Performance

Electronics:
Linearity:
Photometric Stability: <0.0005 Abs/hr
Scale Expansion:
Detector: Photomultiplier S-20 response, standard
S-1 response, optional

Monochromator: Two modified Czerny-Turner
Grating: 600 lines/mm blazed at 300 nm
Wavelength Range: 200 to 825 nm, calibrated
Wavelength Accuracy: ±0.2 nm
Wavelength Resettability: ±0.1 nm
Resolution: <0.3 nm, determined by Hg triplet at 365 nm
Dispersion: 5.5 nm/mm
Slit Width: Bilateral curved slits, continuously adjustable from 0 to 17 nm bandpass; digital readout graduated in 0.02 nm increments
Optical Chopper: Two-speed system, operates at 250 Hz in normal mode and 1000 Hz in kinetic mode
Stray Light: < 0.2% at 200 nm
Response: 22.5 μsec, 50 msec, 165 msec and 2.5 sec to 73% of full scale (Recorder time constant, 300 msec)

Operation

Calibration: Standard samples
Procedure: Manual provided
Training: Required about 4 hours
Maintenance: Factory and field service

Requirements

Power: 115 Vac, 50-60 Hz, 8 amps
Weight: 250 kg (546 lb)
Dimensions: Recorder and optical unit -- 153 cm L x 76 cm D x 37 cm H (60 in. L x 30 in. D x 14-1/2 in. H)
Power supply -- 76 cm L x 61 cm D x 28 cm H (30 in. L x 24 in. D x 11 in. H)

Features

Output: Recorder, 11 in. x 17 in.; automatic wavelength scanner, eight calibrated speeds 0.1 to 20.0 nm/sec and 0.5 to 100 sec/in.

Options:	
Anaerobic Cell	$ 997
Stopped-Flow	$ 3,690
Low Temperature	$ 775
Oxygen Electrode	$ 735
Long Path Cell Holder	$ 145
Solid Sample	$ 2,120
Filter Holder	$ 72
1 x 2 cm Cell Holder	$ 180
Infrared	$ 785

Cost

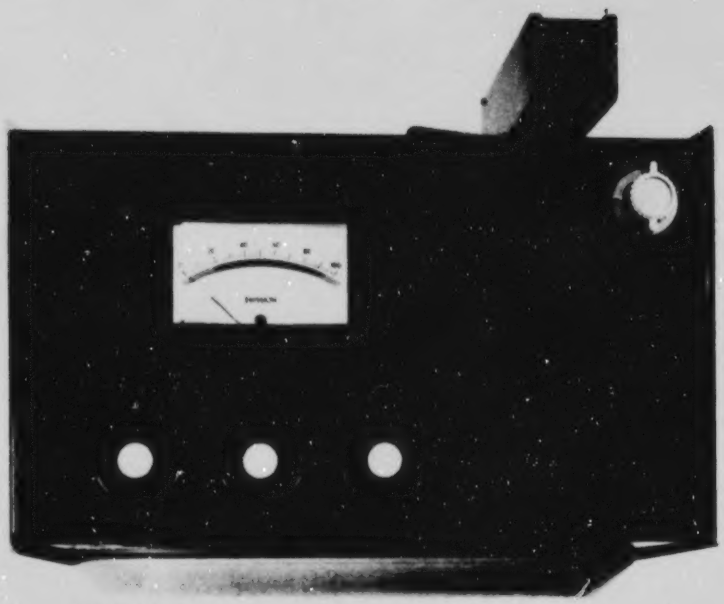
Model DW-2™	$20,895

Address

American Instrument Co.
Division of Travenol Lab
8030 Georgia Ave.
Silver Spring, MD 20910
(301) 589-1727

Filter Fluorometer

Baird Atomic FM-200



Class	Laboratory
Categories	Air: Source, Vehicluar, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Fluorescence
Lower Detectable Limit	
Range	
Interferences	
Multiparameter Capability	
Sampling	Method: Batch Volume: 1.0 ml Capacity: 4 samples/minute

Performance

Electronics:

Linearity:
Stability: 0.5% of full scale per hour
Scale Expansion: None
Detector: 931A Photomultiplier
Zero Drift:
Span Drift:

Monochromator:

Light Source: Phosphor lamps standard; UV lamps optional
Light Filters: Glass or interference types
Wavelength Range: Dependent on lamp and filter types
Bandwidth: 10 nm
Resolution: Dependent on filter type used
Dispersion:
Slit Width:

Operation

Calibration: Standard samples
Procedure: Manual provided
Training:
Unattended Period: None
Maintenance: Service centers throughout the U.S.

Requirements

Power: 110 Vac, 60 Hz, or 220 Vac, 50 Hz, watts
Weight: 13.7 kg (30 lb)
Dimensions: 45.7 cm, 28 cm, 15.3 cm (18" x 11" x 6")

Features

Output: Analog meter, recorder jacks
Options: Flow cells

References

Manufacturer's Bulletin

Cost

Model FM 200 $890.

Address

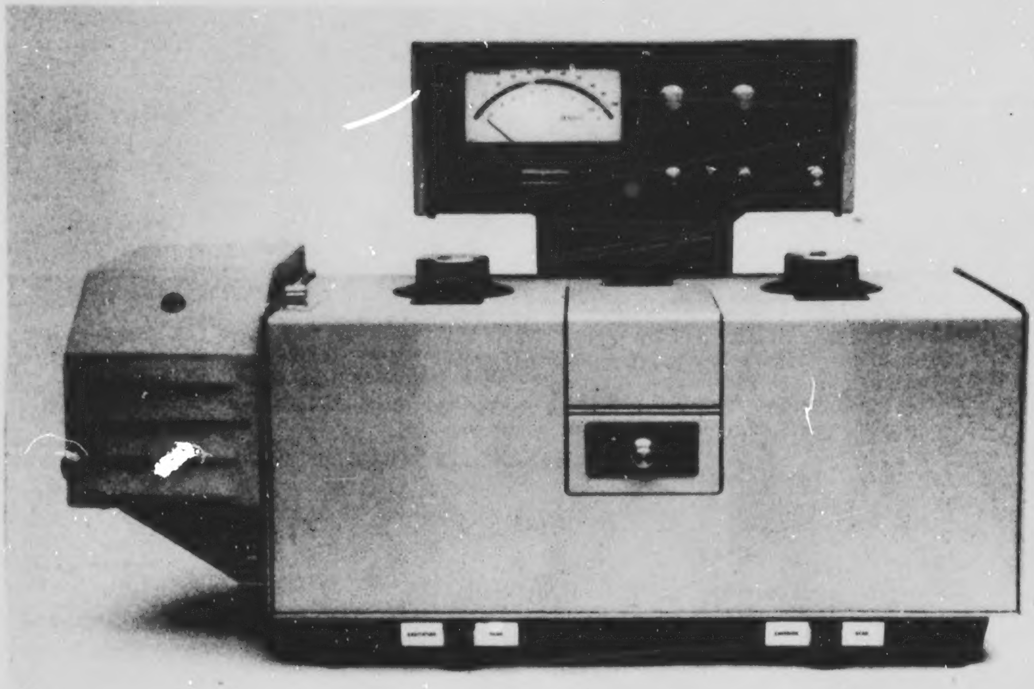
Baird Atomic
125 Middlesex Turnpike
Bedford, MA 01730
(617) 276-6000

Instrument	Wavelength Range (nm)	Wavelength Accuracy (nm)	Wavelength Resolution (nm)	Cost	Remarks
Beckman					
ACTA M-VII	190-800 800-3000	±0.1 ±0.5	< 0.05 < 0.30	$29,200.	
GCA/McPherson					
EU-701-D	185-750 185-1000 (optional)	±0.1	0.1	$ 5,575.	
EU-707	"	"	"	$ 7,425.	
EU-721-D	"	"	"	$ 6,250.	
Micromedic					
MS 2	200-700	±1.0	0.0003A	$ 5,795.	
Perkin-Elmer					
Junior Series	325-825	±1.0	20	$638 to $852	
54	330-835	"	±1	$ 1,894.	
55	325-800 200 (optional)	±1.0	2	$ 3,219.	
295	400-700	±1.0 @ 610 nm		$ 437.	
Pye-Unicam					
SP 1700	190-700 850 (optional)	±0.5	0.1	$ 9,410.	Digital readout
SP 1800	"	"	"	$ 8,410.	Analog readout
Tektronix					
RSS	250-1100	±10 (150 1/mm) ±3 (1200 1/mm)	4 (150 1/mm) 0.4 (1200 1/mm)	$ 12,600.	Silicon vidicon detector
Turner					
110	254-600	Blocking filters	Blocking filters	$ 1,295.	Filter photometer, manual
111	"	"	"	$ 1,820.	Filter photometer, automatic
330	335-710	±2.0	9.0	$ 645.	Spectrophotometer
350	"	"	"	$ 795.	"
430	300-700	"	15 (Excitation) 15 and 60 (Emission)	$ 4,185.	Spectrofluorometer
510	Interference filters			$ 3,950.	Flame photometer
Varian					
Cary 17	186-2650	±0.4	0.1 (UV-Vis) 0.3 (IR)	$ 29,990.	Prism and grating
Cary 118A	185-800		0.03 @ 200 nm 0.1 @ 350 nm	$ 11,900.	Manual
Cary 118B	"		"	$ 15,525.	Ratio recording

(Continued)

Ultraviolet/Visible Spectrophotometer

Baird Atomic, Fluoripoint FP-100

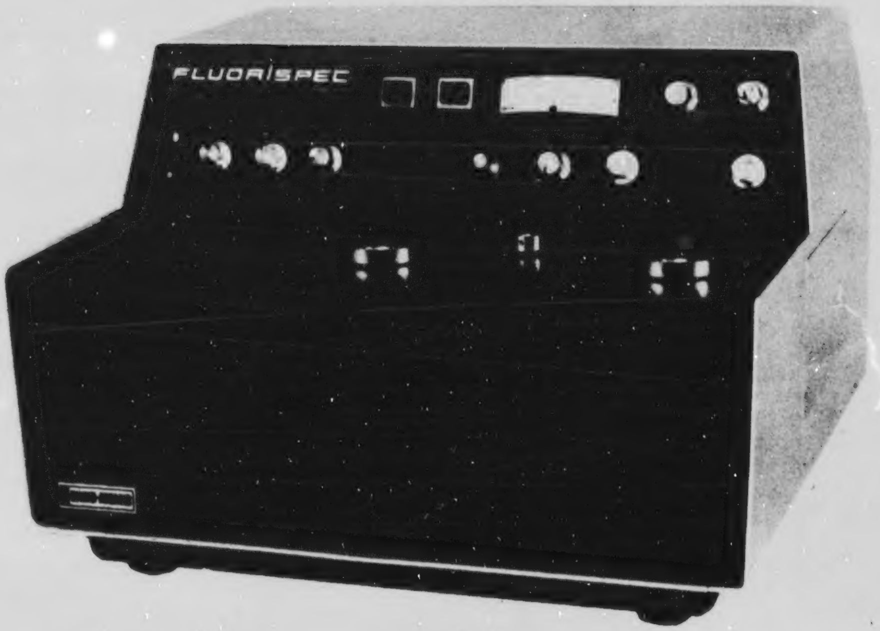


Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Single beam, analog readout, calibrated from 1-100% (absorbance) and 0-2 "optical density".
Lower Detectable Limit	
Range	Emission: 0-100% Optical Density: 0-2
Interferences	
Multiparameter Capability	Excitation and fluorescence wavelength scanning
Sampling	Method: Batch Volume: 1.0 ml (4 µl optional) Capacity:

Performance	Electronics: Linearity: Stability: < 1% of full scale per hour Scale Expansion: .1x, 1x, 10x Detector: EMI 978LA Photomultiplier Zero Drift: Span Drift: Scanning Speed: Automatic or manual (1 nm/sec auto) Monochromator: Czerny Turner Grating: Excitation blazed at 300 nm Emission blazed at 500 nm Resolution: 2 nm Dispersion: Slit Width: Independently variable, 10 and 20 nm standard Stray Light:
Operation	Calibration: Standard solutions Procedure: Manual; automatic scanning Training: Unattended Period: Maintenance: Service centers throughout the U.S.
Requirements	Power: 110 Vac, 60 Hz, 10 Amps Weight: Dimensions: 65 cm x 42 cm x 38 cm (25.5" x 16.5" x 15")
Features	Output: Analog meter Options: Recorder digital display/printout Polarization Accessory Microsampler Solid sampler
References	Manufacturer's Bulletin
Cost	Model FP-100 $5874.
Address	Baird Atomic 125 Middlesex Turnpike Bedford, MA 01730 (617) 276-6000

Spectrofluorometer

Baird Atomic, SF-100

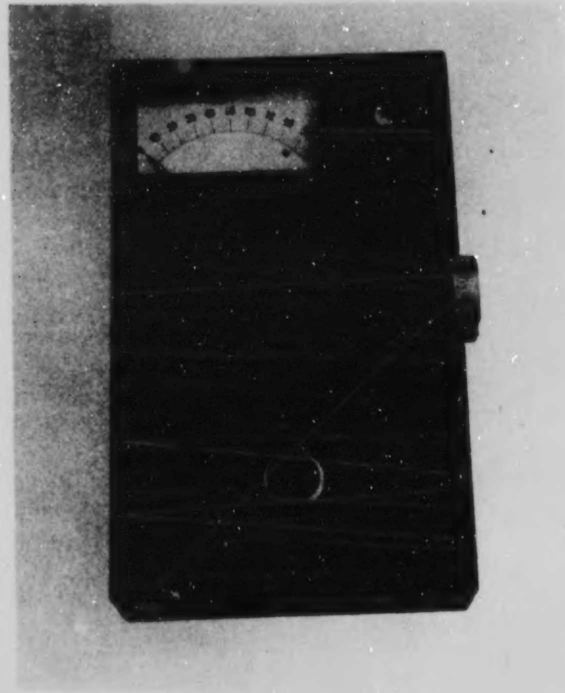


Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Chemiluminescent; dual beam, double monochromator
Lower Detectable Limit	
Range	1 ppb
Interferences	
Multiparameter Capability	Emission and excitation wavelength scanning
Sampling	Method: Batch and automatic Volume: 1.0 ml (optional 4 μl) Capacity: Temperature Compensation:

Performance	Electronics: Solid state Linearity: Stability: 1% of full scale per hour Scale Expansion: .1x, 1x, 10x, 100x Lamp: 150 W Xenon, Xenon-Mercury optional Detector: 1P28 Photomultiplier, RCA, variable voltage from 185 - 1200 Vdc Zero Drift: Span Drift: Monochromator: Dual double grating Grating: x mm, excitation grating blazed at 300 nm x mm, emission grating blazed at 500 nm Wavelength Range: 220-700 nm, standard 220-1200 nm, optional Wavelength Accuracy: 2 nm Bandwidth: Resolution: 2 nm Dispersion: Slit Width: Four independently variable slits, 3 positions each, 1.5, 6, or 21 nm
Operation	Calibration: Standard samples Procedure: Manual or automatic wavelength scanning Training: Unattended Period: None Maintenance: Service centers throughout U.S.
Requirements	Power: 110 Vac, 60 Hz, or 220 V, 50 Hz, 1100 watts Weight: 84.5 kg (186 lb) Dimensions: 53.5 cm, 57 cm, 38 cm (21" x 22.5" x 15")
Features	Automatic and manual scanning Output: Analog meter, recorder output, digital display, output jack Options: Phosphoroscope Low Temperature Analyzer TLC Scanners (Plate and Strip) Extended Wavelength Range; Solid Sample Holder Flow Through Cells
References	Manufacturer's Bulletin
Cost	Model SF-100 $8,600.
Address	Baird Atomic 125 Middlesex Turnpike Bedford, MA 01730 (617) 276-6000

Colorimeter/Spectrophotometer

Bausch & Lomb Mini Spec ™ 20



Class	Portable, battery powered
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste, Process Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Single beam, ratio indicating grating monochromator, read out linear in % transmittance, overlays for absorbance, blank overlays for concentration
Lower Detectable Limit	Depends on chemical method and cell path length. Limits in the parts per billion range can be achieved.
Range	ppb to percent - depends on chemical method and pathlength
Interferences	Depends on chemical method
Multiparameter Capability	Spectrophotometric, turbidimetric, color
Sampling	Method: Batch, 0.5 in test tubes, flat bottom cuvettes, 10 mm or 25 mm rectangular cuvettes

Minimum Volume of Solution:

Cuvette	Min. Vol.
1/2" test tube	1.3 ml
1/2" vial	1.8 ml
10 mm square	1.6 ml
25 mm	3.2 ml

Performance	Electronics: Meter Linearity: ±2 T Stability: Scale Expansion: Detector: Photo Resistor Zero Drift: Span Drift: Warm-up: 10 seconds Monochromator: Grating: 600 grooves/mm Wavelength Range: 400-700 nm Wavelength Accuracy: ±3 nm at 546 nm Wavelength Repeatability: 1 nm Spectral Bandwidth: 20 nm Resolution: Dispersion: Slit Width: Pathlength: 1 mm to 25 mm
Operation	Calibration: Standard samples Temperature Range: Operating, 5°C to 40°C Storage, -5°C to 70°C Training: Manual available Unattended Period: Not automated Maintenance: Sample compartment is removable and waterproof. One year warranty.
Requirements	Power: Battery operated, 3 hours of continuous use or 115 Vac, 50-60 Hz, or 230 Vac, 50-60 Hz, or 12 Vdc (automobile cigarette lighter) adapters Weight: 0.45 kg (1 lb) Dimensions: 15 cm, 9 cm, 5 cm (6 in., 3.5 in., 2 in.)
Features	Output: Analog meter; standard 500 mVdc nominal at 100% T into 10^6 ohms Recorder output jack
References	Manufacturer's specifications
Cost	Mini Spec™-20 $495
Address	Bausch & Lomb, Inc. Analytical Systems Division 820 Linden Ave. Rochester, NY 14625 (716) 385-1000

Colorimeter/Spectrophotometer

Bausch and Lomb, Spectronic® 20

Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste, Process Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Single beam, ratio indicating, either transmittance or absorption mode. As a spectrophotometer, grating selects wavelength and gives absorption measurement. As a colorimeter, gives readings of optical density or percent transmittance.
Lower Detectable Limit	Depends on chemical method and cell path length. Limits in the part per billion range can be achieved.
Range	ppb to percent
Interferences	Depends on chemical method
Multiparameter Capability	Spectrophotometric, turbidimetric, color, reflectance
Sampling	Method: Batch or semi-automatic

Minimum Volume of Solution:

test tube diameter	sample volume
0.50 in.	3 ml
0.75 in.	5 ml
1.0 in.	8 ml
microcuvette	0.2 ml

Capacity: 5 samples/minute with flow through cuvette

Performance

Electronics:
Meter Linearity: ±1% of full scale
Stability: 1% of full scale
Scale Expansion:
Detector: Phototubes
Zero Drift:
Span Drift:
Warm-up Time: 15 minutes

Monochromator:
Grating: 600 grooves/mm
Wavelength Range: 340-950 nm
Wavelength Accuracy: 2.5 nm
Wavelength Repeatability: 1.0 nm
Resolution:
Dispersion:
Spectral Bandwidth: 20 nm

Operation

Calibration: Standard samples
Training: Manual available
Unattended Period: Not automated
Maintenance: Minimal, liquids can be drained through door in bottom of sample compartment

Requirements

Power: 105 to 125 Vac, regulated model, 100 watts
120 Vac, non-regulated model, 40 watts
Weight: About 12 kg (27 lb)
Dimensions: 41 cm x 33.5 cm x 20 cm (16.25" x 13.25" x 8.25")

Features

Output: Analog; 0-1 Vdc, regulated model only

Options:	
Digital display, Model DR-37	$300
Semi-automatic flow thru cuvette	$437
Reflectance, accessory	$625
Microcell assembly	$122
Short path flow thru	$185

References

Manufacturer's specifications

Cost

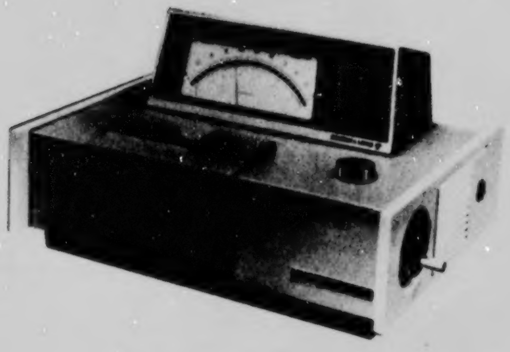
Spectronic® 20, standard model 33-31-71	$525
Spectronic® 20, regulated model 33-31-72	$595

Address

Bausch and Lomb, Inc.
Analytical Systems Division
820 Linden Ave.
Rochester, NY 14625
(716) 385-1000

Colorimeter/Spectrophotometer

Bausch & Lomb, Spectronic® 70



Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Single beam, ratio indicating, either transmittance or absorption mode. As a spectrophotometer, grating selects wavelength and gives absorption measurement. As a colorimeter, gives readings of optical density or percent transmittance.
Lower Detectable Limit	Depends on chemical method and cell path length
Range	Absorbance: 0-2.0, log Transmittance: 0-100%
Interferences	Depends on chemical method
Multiparameter Capability	Spectrophotometry, colorimetry
Sampling	Method: Batch Minimum Volume of Solution:

	Pathlength	Min. Volume
Test tube	10 mm	2.5 ml
Test tube	20 mm	10.0 ml
Short path cuvette	1 mm	0.02 ml
Short path cuvette	2 mm	0.04 ml
Short path cuvette	5 mm	1.0 ml
Cuvette	10 mm	2.0 ml
Long path cell	50 mm	14.2 ml
Long path cell	100 mm	28.4 ml

Performance

Electronics:
Meter Linearity: ±1% of full scale
Stability: Better than 2.0% per day
Scale Expansion: None
Detector: Phototubes
Zero Drift: <0.2% per day (T only)
Span Drift:

Monochromator:
Grating: 1200 grooves/mm, blazed at 300 nm
Wavelength Range: 325-925 nm
Wavelength Accuracy: Better than 1.0 nm
Wavelength Repeatability: Better than 0.2 nm
Spectral Bandwidth: 8.0 nm
Photometric Linearity: Better than 0.5%
Photometric Noise: Less than 0.1%

Operation

Calibration: Standard samples
Training: Manual provided
Unattended Period: None
Maintenance: One year warranty, service contract available

Requirements

Power: 100, 120, 230, 240 Vac, 50-60 Hz
Weight: 35 lb
Dimensions: 43 cm W, 23 cm H, 34 cm D (17" W, 9" H, 13.5" D)

Features

Output: Analog, 0-1 Vdc nominal

Options:	Multiple sample compartment	$180
	Single sample compartment	$100
	Thermo regulated multiple sample holder	$120
	DR-37 digital readout	$300

References

Manufacturer's specifications

Cost

Spectronic® 70	$875

Address

Bausch & Lomb, Inc.
Analytical Systems Division
820 Linden Ave.
Rochester, NY 14625
(716) 385-1000

Colorimeter/Spectrophotometer

Bausch & Lomb, Spectronic® 88

Class

Laboratory

Categories

Air: Source, Vehicular, Ambient
Water: Fresh, Saline, Waste
Biomedical: Blood, Tissue, Serum, Urine

Principle of Operation

Single beam, ratio indicating, either transmittance or absorption mode. As a spectrophotometer, grating selects wavelength and gives absorption measurement. As a colorimeter, gives readings of optical density or percent transmittance.

Lower Detectable Limit

Depends on chemical method and cellpath length

Range

Absorbance: 0-2.0, linear
Transmittance: 0-100%
Concentration: 0-2000
1X to 3X multiplier

Interferences

Depends on chemical method

Multiparameter Capability

Spectrophotometry, colorimetry

Sampling

Method: Batch or semi-automatic
Minimum Volume of Solution:

	Pathlength	Min. Volume
Test tube	10 mm	2.5 ml
Test tube	20 mm	10.0 ml
Short path cuvette	1 mm	0.02 ml
Short path cuvette	2 mm	0.04 ml
Short path cuvette	5 mm	1.0 ml
Cuvette	10 mm	2.0 ml
Long path cell	50 mm	14.2 ml
Long path cell	100 mm	28.4 ml

Capacity: With semiautomatic micro flow thru compartment approximately 5 samples per minute may be analyzed.

Performance

Electronics:
Meter Linearity: ±1% of full scale
Stability: Better than 0.004 A near 0 A
Better than 0.010 A near 1 A
Better than 0.20 A near 2 A
Scale Expansion: 1X to 3X multiplier
Detector: Phototubes
Zero Drift: <0.2% per day (T only)
Span Drift:

Monochromator:
Grating: 1200 grooves/mm, blazed at 300 nm
Wavelength Range: 325-925 nm
Wavelength Accuracy: Better than 1.0 nm
Wavelength Repeatability: Better than 0.2 nm
Spectral Bandwidth: 8.0 nm
Dispersion:
Photometric Linearity: Better than 0.5%
Photometric Noise: Less than 0.1%

Operation

Calibration: Standard samples
Training: Manual provided
Unattended Period: None
Maintenance: Service centers in the U.S.

Requirements

Power: 100, 115, 220, 240 Vac, 50-60 Hz
Weight: 35 lb
Dimensions: 43 cm W, 23 cm H, 34 cm D (17" W, 9" H, 13.5" D)

Features

Output: Analog meter 0-1 Vdc nominal

Options:	Semi-automatic flow thru cuvette	$ 495
	Multiple sample compartment	$ 180
	Single sample compartment	$ 100
	Thermo regulated multiple sample holder	$ 120
	DR-37 digital readout	$ 300
	Automatic cell positioner	$1095

References

Manufacturer's specifications

Cost

Spectronic® 88	$1195

Address

Bausch & Lomb, Inc.
Analytical Systems Division
820 Linden Ave.
Rochester, NY 14625
(716) 385-1000

Colorimeter/Spectrophotometer

Bausch & Lomb, Spectronic® 100

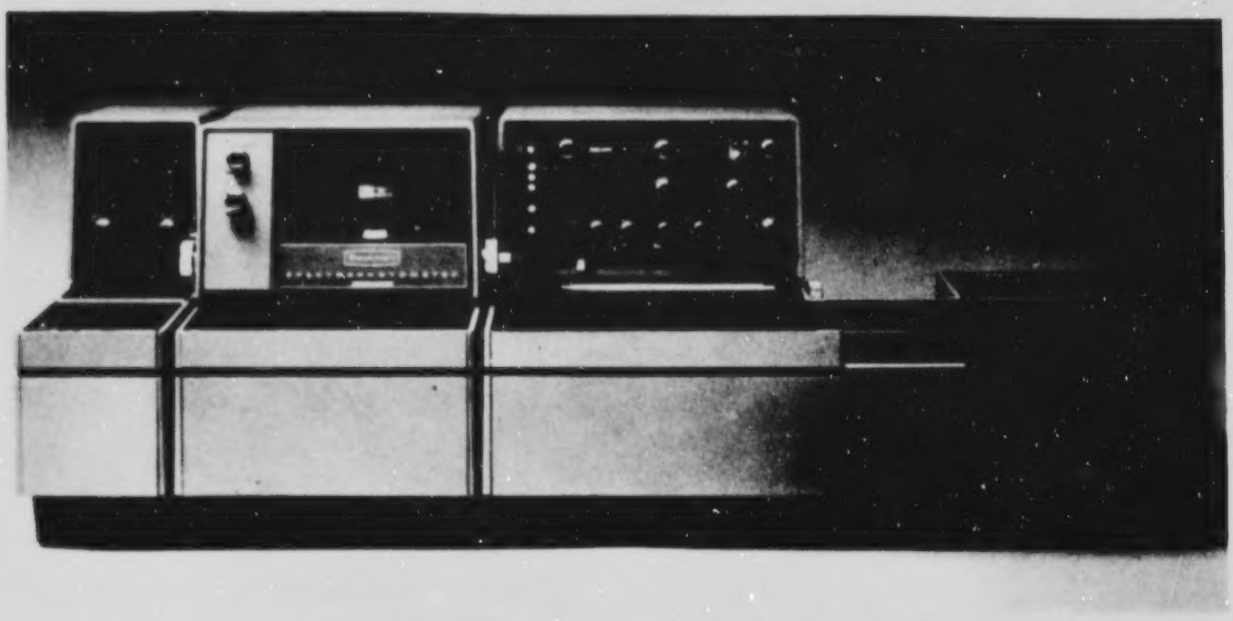
Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Single beam, ratio indicating, either transmittance or absorption mode. As a spectrophotometer, grating selects wavelength and gives absorption measurement. As a colorimeter, gives readings of optical density or percent transmittance.
Lower Detectable Limit	Depends on chemical method and cell path length
Range	Absorbance: 0-2.0, linear, digital Transmittance: 0-100%, digital Concentration: 0-2000 digital with selectable decimal
Interferences	Depends on chemical method
Multiparameter Capability	Spectrophotometry, colorimetry
Sampling	Method: Batch or semi-automatic Minimum Volume of Solution:

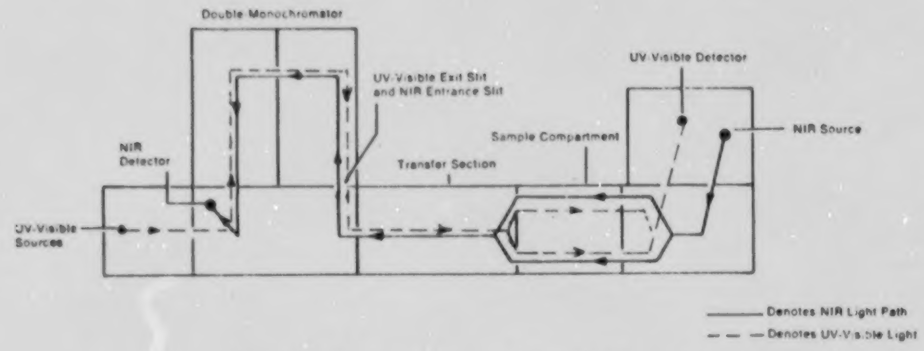
	Pathlength	Min. Volume
Test tube	10 mm	2.5 ml
Test tube	20 mm	10.0 ml
Short path cuvette	1 mm	0.02 ml
Short path cuvette	2 mm	0.04 ml
Short path cuvette	5 mm	1.0 ml
Cuvette	10 mm	2.0 ml
Long path cell	50 mm	14.2 ml
Long path cell	100 mm	28.4 ml

Capacity: With semi-automatic micro flow thru compartment approximately 5 samples per minute may be analyzed.

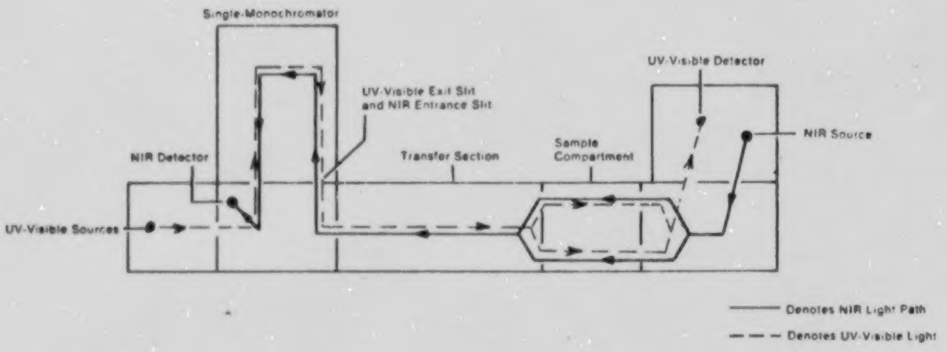
Ultraviolet/Visible-Near Infrared, Spectrophotometer

Beckman, ACTA M Series




Double Monochromator
UV-Visible Exit Slit and NIR Entrance Slit
UV-Visible Detector
NIR Source
Sample Compartment
NIR Detector
Transfer Section
UV-Visible Sources
Denotes NIR Light Path
Denotes UV-Visible Light

Optical Block Diagram of ACTA® MVII


Single-Monochromator
UV-Visible Detector
UV-Visible Exit Slit and NIR Entrance Slit
NIR Source
NIR Detector
Transfer Section
Sample Compartment
UV-Visible Sources
Denotes NIR Light Path
Denotes UV-Visible Light

Optical Block Diagram of ACTA® MIV

Performance

Electronics:
Photometric Linearity: Better than 0.2% T
Better than .001 A at 0 A
Better than .003 A at 1 A
Better than .007 A at 2 A
Photometric Noise: Less than 0.1% T
Less than .001 A at 0 A
Less than .003 A at 1 A
Less than .006 A at 2 A
Stability: Better than 0.2%/hr in T
Better than 0.001 A/hr in A
Detector: Phototubes
Zero Drift: <0.2% per day (T only)

Monochromator:
Grating: 1200 grooves/mm, blazed at 300 nm
Wavelength Range: 325-925 nm
Wavelength Accuracy: Better than 1.0 nm
Wavelength Repeatability: Better than 0.2 nm
Spectral Bandwidth: 8.0 nm

Operation

Calibration: Built-in calibration system
Training: Manual provided
Unattended Period: Manual, semi-automatic, automatic
Maintenance: Service centers in U.S.

Requirements

Power: 100, 120, 330, 240 Vac, 50-60 Hz
Weight: 1.6 kg (35 lb)
Dimensions: 43 cm W, 23 cm H, 34 cm D (17" W, 9" H, 13.5" D)

Features

Output: Digital display, 0-2 Vdc nominal analog output; BCD output

Options:	Semi-automatic flow thru cuvette	$ 495
	Multiple sample compartment	$ 180
	Single sample compartment	$ 100
	Thermo regulated multiple cell holder	$ 120
	Automatic cell positioner	$1095

References

Manufacturer's specifications

Cost

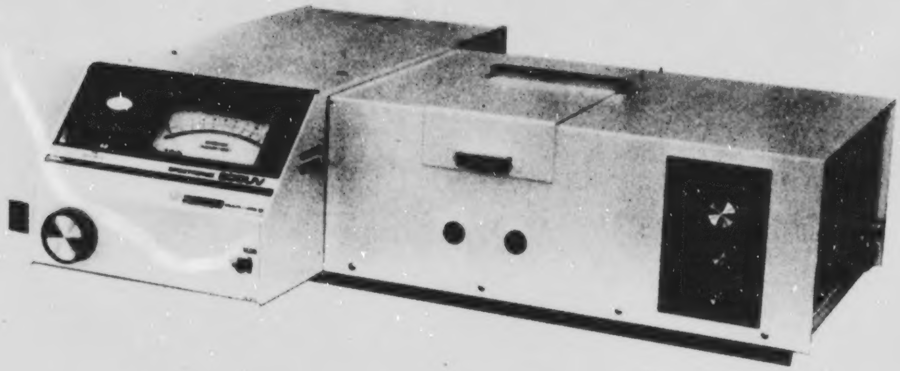
Spectronic® 100	$2195

Address

Bausch & Lomb, Inc.
Analytical Systems Division
820 Linden Ave.
Rochester, NY 14625
(716) 385-1000

Ultraviolet/Visible Spectrophotometer

Bausch & Lomb, Spectronic® 200



Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Double beam, ratio indicating, either transmittance or absorption mode
Lower Detectable Limit	Depends on chemical method and cell path length
Range	Absorbance: 0-1.00, 0-2.00, linear Transmittance: 0-100%
Interferences	Depends on chemical method
Multiparameter Capability	Spectrophotometry; turbidity; reflectance
Sampling	Method: Batch or semi-automatic Volume: Dependent upon sample cell used Compartment: 11 cm W, 17 cm D, 13.5 cm H Maximum Optical Path Length of Cell: 100 mm Temperature Compensation: Water jacket cells or constant temperature cell holders

Performance

Electronics: Solid state
Linearity:
Stability: Better than 0.005 A per day
Scale Expansion: Via accessory recorder
Detector: R-446 photomultiplier
Photometric Accuracy: ±0.005 (at 0.4 Abs)
Photometric Reproducibility: ±0.2% T
Span Drift: Baseline flatness, ±1.0%
Scan Speed: 60, 120, 240, 380 nm/min (60 Hz), 30 nm/min optional

Monochromator: Czerny-Turner
Grating: 1200 gr/mm, blazed at 200 nm
Light Source: Deuterium and tungsten lamps
Wavelength Range: 190-800 nm
Wavelength Accuracy: ±0.5
Wavelength Reproducibility: ±0.2 nm
Spectal Bandwidth: 0.25, 0.5, 1.0, and 2.0 nm
Resolution:
Dispersion:
Stray Light: Less than 0.1% at 220 nm

Operation

Calibration: Didymium and 10% neutral density filters
Procedure: Manual operation
Training: Operators' manual
Unattended Period: Manual operation
Maintenance: 1-year warranty; service contract available

Requirements

Power: 120 V, 60 Hz, 300 watts
Weight: 57 kg (125 lb)
Dimensions: 85 cm W, 60 cm D, 21 cm H (33.4" W, 23.6" C, 8.2" H)

Features

Output: Analog 100 mV

Options:	Y-T recorder	$ 895
	Reflectance sphere	$1,000
	Four-place turret cell holder	$ 350
	Opal glass attachment	$ 225
	Cylindrical cell holder	$ 110
	Constant temperature cell holder	$ 350

Cost

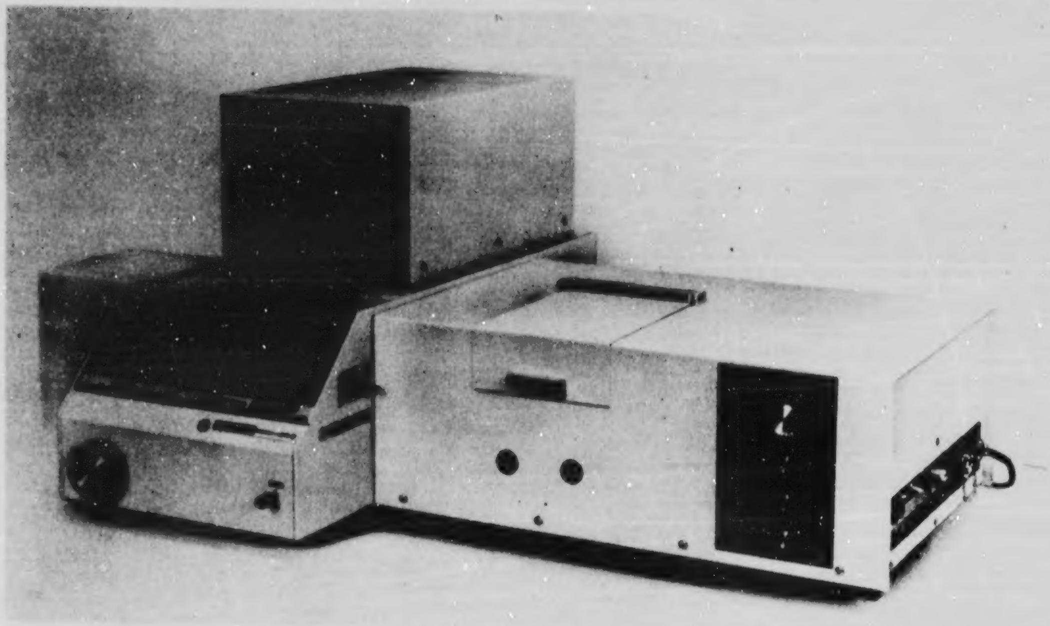
Spectronic 200 UV	$4,895

Address

Bausch and Lomb, Inc.
Analytical Systems Div.
820 Linden Ave.
Rochester, NY 14625
(716) 385-1000

Ultraviolet/Visible Spectrophotometer

Bausch & Lomb, Spectronic® 210



Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Double beam, dual lamp, mechanical chopper, grating, single detector, digital readout
Lower Detectable Limit	Depends on chemical method and cell pathlength
Range	Absorbance: 0-2.00, 0-0.2, linear Transmittance: 0-100%, 0-10%, linear Concentration: 0-1999, selectable decimal point
Interferences	Depends on chemical method
Multiparameter Capability	Spectrophotometry, reflectance
Sampling	Method: Batch Volume: Dependent upon sample cell used Temperature Compensation: Water jacketed cells or constant temperature cell holder Maximum Optical Path Length of Cell: 100 mm

Performance

Electronics: Solid state
Linearity:
Stability: Better than 0.005 A per day
Scale Expansion: Via accessory recorder
Light Source: Tungsten and deuterium lamps
Detector: R446 photomultiplier
Photometric Accuracy: ±0.005 A (at 0.4 Abs); 0.5% T
Photometric Reproducibility: ±0.2% T
Span Drift: 100% flatness, ±1.0%

Monochromator: Czerny-Turner
Grating: 1200 grooves/mm, blazed at 200 nm
Wavelength Range: 190-900 nm
Wavelength Accuracy: ±0.5 nm
Wavelength Repeatability: ±0.2 nm
Wavelength Scanning: 60, 120, 240 or 480 nm/min, 30 nm/min optional
Bandwidths: 0.25, 0.5, 1.0, 2.0 and 5.0 nm
Dispersion:
Stray Light: < 0.1% at 220 nm

Operation

Calibration: Didymium and 10% neutral density filters
Procedure: Manual
Training: Operators' manual
Unattended Period: Manual operation
Maintenance: 1-year warranty, service contract available

Requirements

Power: 120 Vac, 60 Hz, 300 watts
Weight: 56.7 kg (125 lb)
Dimensions: Spectrometer - 85 cm W, 60 cm D, 21 cm H (33.4" x 23.6" x 8.2")
Power Supply - 21 cm W, 35 cm D, 17 cm H (8.2" x 13.7" x 6.7")

Features

Output: Analog 100 mV

Options:	
T-Y flatbed recorder	$ 895
4-place turret cell holder	$ 350
Opal glass attachment	$ 225
Cylindrical cell holder	$ 110
Constant temperature cell holder	$ 350
DP-110 data processor	$2,195
Reflectance sphere	$1,000

References

Manufacturer

Cost

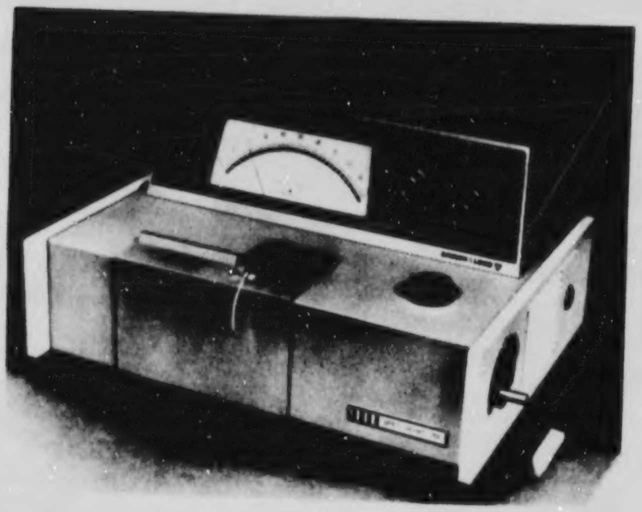
Spectronic® 210 digital	$6,000

Address

Bausch & Lomb, Inc.
Analytical System Division
820 Linden Ave.
Rochester, NY 14625
(716) 385-1000

Spectrophotometer

Bausch and Lomb, Spectronic® 700



Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Single beam, ratio indicating UV-visible spectrophotometer reading out in transmittance (0-100%), absorbance (0-2 A) and 2 modes of concentration on an 8" meter
Minimum Detectable Sensitivity	Depends on chemical method and pathlength of cell
Range	Transmittance: 0-100.0% Absorbance: 0-2.0 Concentration: 0 to maximum value
Interferences	Depends on chemical method
Multiparameter Capability	Spectrophotometry
Sampling	Method: Batch, semi-automatic, or automatic

Minimum Volume of Solution:

	Pathlength	Min. Volume
Test tube	10 mm	2.5 ml
Test tube	20 mm	10.0 ml
Short path cuvette	1 mm	0.02 ml
Short path cuvette	2 mm	0.04 ml
Short path cuvette	5 mm	1.0 ml
Cuvette	10 mm	2.0 ml
Long path cell	50 mm	14.2 ml
Long path cell	100 mm	28.4 ml

Capacity: With semi-automatic Micro Flow thru compartment approximately 5 samples per minute may be analyzed.

Performance

Electronics: Solid State
Photometric Linearity: Better than 0.004 A at 0.4 A
Stability: Less than 0.002 A near 0 A
Scale Expansion: 3x in concentration
Detector: 2 phototubes
Zero Drift: Less than 0.1% per day
Warm-up Time: 15 minutes

Monochromator:
Grating: 1200 grooves/mm, blazed at 300 nm
Wavelength Range: 200-950 nm
Wavelength Accuracy: Better than 1.0 nm
Wavelength Precision: Better than 0.3 nm
Stray Light: Less then 0.5% at 220 nm

Spectral Band Width: 2.0 nm

Operation

Calibration: Built-in electronic calibration check
Deuterium lines for wavelength calibration
Manual includes procedure for 34 clinical calibrations:

1. Amylase Activity of Serum or Urine
2. Bilirubin in Serum
3. Bromide in Blood
4. Bromosulphthalein (BSP) in Serum
5. Calcium in Serum
6. Chloride in Serum, Cerebrospinal Fluid or Urine
7. Cholesterol (total in Serum)
8. Creatinine in Serum or Urine
9. Fibrinogen in Plasma
10. Glucose in Blood, Plasma, Serum, or Cerebrospinal Fluid -- (Copper Reduction Procedure)
11. Glucose in Blood, Plasma, Serum, or Cerebrospinal Fluid -- (Enzymatic Procedure)
12. Hemoglobin (as Cyanmethemoglobin) in Blood
13. Hemoglobin (as Oxyhemoglobin) in Blood
14. Iron in Serum: Iron-Binding Capacity of Serum
15. Lactic Dehydrogenase Activity (LDH) of Serum -- (Colorimetric Procedure)
16. Lactic Dehydrogenase Activity (LDH) of Serum -- (at 340 mu)
17. Magnesium in Serum
18. Nonprotein Nitrogen (NPN) in Blood or Serum
19. Phenolsulfonphthalein (PSP) in Urine
20. Phosphatase Activity (Total Acid, Prostatic Acid, and Alkaline) of Serum
21. Phosphorus (Inorganic) in Serum or Urine
22. Proteins (Total) in Cerebrospinal Fluid
23. Proteins (Total, Albumin, and Globulins) in Serum
24. Proteins (Total) in Urine
25. Salicylate in Blood
26. Sulfonamides (Sulfa Drugs) in Blood
27. Thymol Turbidity Test
28. Transaminase Activity (GOT and GPT) of Serum -- (Colorimetric Procedure)
29. Transaminase Activity (GOT and GPT) of Serum -- (at 340 mu)
30. Urea in Blood, Serum or Urine -- (Dialetyl Monoxime Procedure)
31. Urea in Blood, Serum or Urine -- (Nesslerization Procedure)
32. Uric Acid in Serum or Urine
33. Urobilinogen in Feces or Urine
34. Xylose in Urine (Xylose Tolerance Test)

Training: Operators' manual
Unattended Period: Depends on system set up
Maintenance: 1-year warranty; service contract available

Requirements

Power: 100, 115, 220, 240 V, 50/60 Hz, watts
Weight: 18.7 kg (41 lb)
Dimensions: 42.5 cm W x 25 cm H x 38.8 cm D (17" W x 10" H x 15-1/2" D)

Features

Analog Output: 0-1 V nominal

Accessories:	10" Strip Chart Recorder	$ 395
	DR-37 Digital Readout	$ 300

References

Manufacturer's Specifications

Cost

Spectronic® 700	$2,600
Single sample compartment	$ 100
Multiple sample compartment	$ 180
Semi-automatic flow thru compartment	$ 495
Automatic cell positioner	$1,095

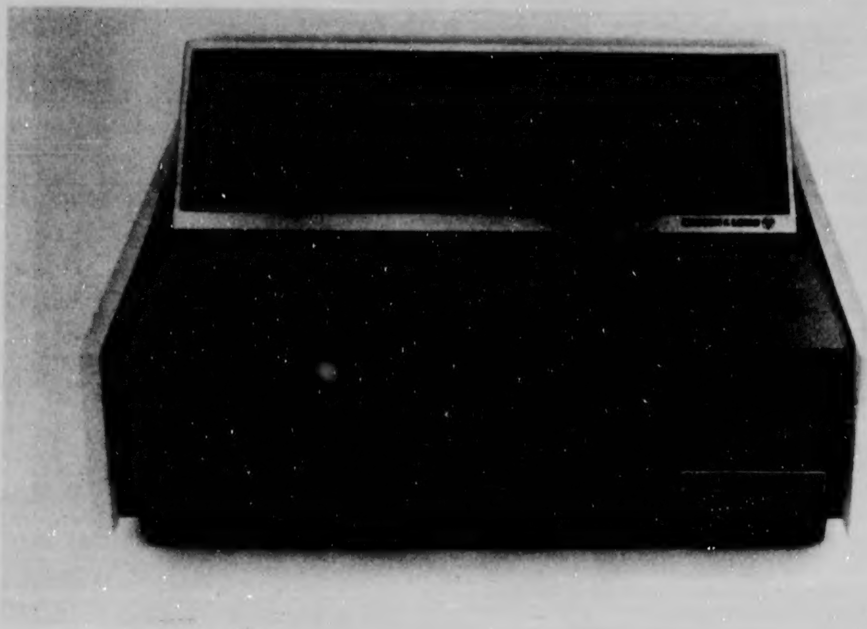
Address

Bausch and Lomb, Inc.
Analytical Systems Division
820 Linden Avenue
Rochester, NY 14625
(716) 385-1000

H2O-MET
UV-Visible
Bausch & Lomb 9
Sept. 1975

Spectrophotometer

Bausch and Lomb, Spectronic® 710



Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Single beam, ratio indicating UV-visible spectrophotometer that reads out results in transmittance, absorbance, or concentration on a 4-place digital readout
Lower Detectable Limit	Depends on chemical method and cell path length
Range	Absorbance: 000.0 - 2.000 Digital Transmittance: 000.0 - 100.0 Digital Concentration: 0000 - 2000 Digital
Interferences	Depends on chemical method
Multiparameter Capability	Spectrophotometry, color
Sampling	Method: Batch, semi-automatic, or automatic Minimum Volume of Solution:

	Pathlength	Min. Volume
Test tube	10 mm	2.5 ml
Test tube	20 mm	10.0 ml
Short path cuvette	1 mm	0.02 ml
Short path cuvette	2 mm	0.04 ml
Short path cuvette	5 mm	1.0 ml
Cuvette	10 mm	2.0 ml
Long path cell	50 mm	14.2 ml
Long path cell	100 mm	28.4 ml

Capacity: With semi-automatic Micro Flow thru compartment approximately 5 samples per minute may be analyzed.

Performance

Electronics: Solid state
Photometric Linearity: Better than 0.002 A near 0.4 A
Stability: Better than 0.001 A near 0.000 A
Scale Expansion: 3X in concentration
Detector: 1 phototube; 1 solid state detector
Zero Drift: Less than 0.2% per day
Warm-up Time: Less than 15 minutes

Monochromator:
Grating: 1200 grooves/mm, blazed at 3000 Å
Wavelength Range: 200 nm-1000 nm
Wavelength Accuracy: Better than 1.0 nm
Wavelength Precision: Better than 0.3 nm
Spectral Band Width: 2.0 nm
Stray Light: Less than 0.5% at 220 nm

Operation

Calibration: Deuterium lines for wavelength calibration
Training: Operators' manual
Unattended Period: Manual, semi-automatic, automatic
Maintenance: 1-year warranty; service contract available

Requirements

Power: 100, 115, 220, 240 V, 50/60 Hz, watts
Weight: 18.7 kg (41 lb)
Dimensions: 42.5 cm W x 25 cm H x 38.8 cm D (17" Wx 10" H x 15-1/2" D)

Features

Analog Output: 0-2 V nominal; BCD

Accessories: 10" Strip Chart Recorder	$ 395
DP-110 Data Processor	$2,195

References

Manufacturer's specifications

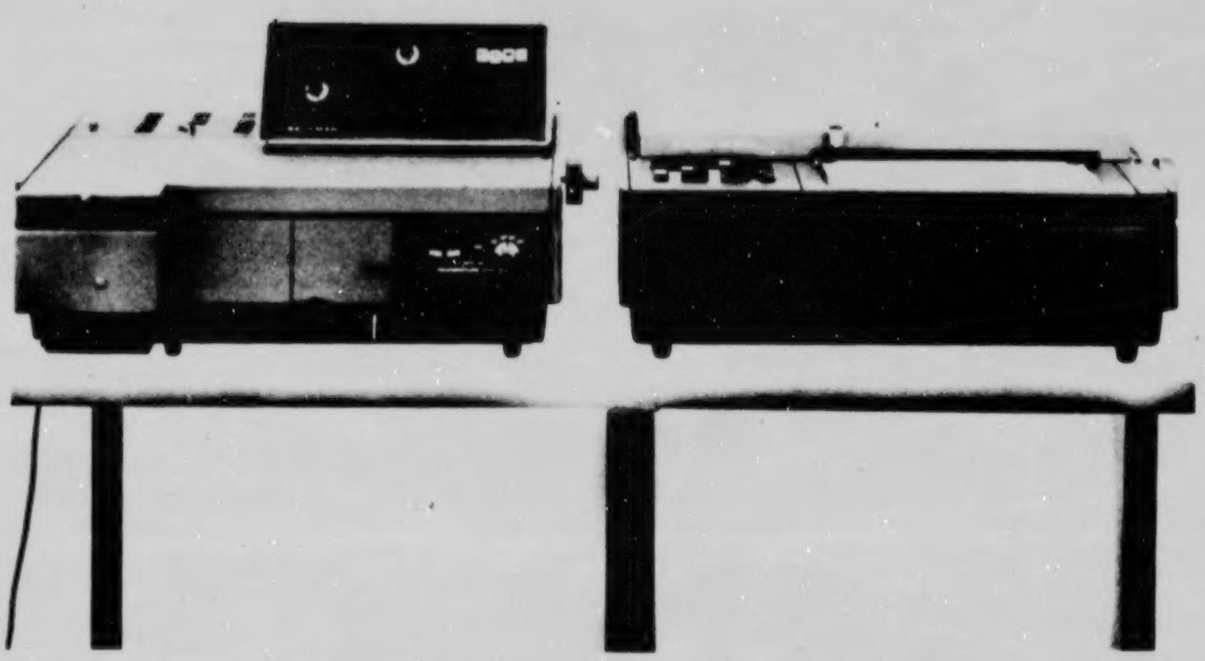
Cost

Spectronic® 710	$3,000
Single sample compartment	$ 100
Multiple sample compartment	$ 180
Semi-automatic flow thru compartment	$ 495
Automatic cell positioner	$1,095

Address

Bausch and Lomb, Inc.
Analytical Systems Division
820 Linden Ave.
Rochester, NY 14625
(716) 385-1000

Ultraviolet/Visible Spectrophotometers
Beckman, Models 24, 25 and 26



Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Double beam, digital readout of absorbance, concentration or differential measurements
Lower Detectable Limit	1 - 10 ppb
Range	0-2.00 Absorption; 0-8000 Concentration
Interferences	
Multiparameter Capability	
Sampling	Method: Automatic, sipper accessory (1 ml vol) Volume: 4 ml Capacity: 6-10 samples/minute Temperature controlled sample compartment: Fixed temperatures: 30°C, 32°C, 37°C Accuracy: ±0.25°C Control: ±0.1°C

Performance

Electronics: Solid state
Linearity:
Stability: 0.0004 Abs/Hr
Accuracy: ±0.5% of value or 0.001 Abs. whichever is greater
Scale Expansion: 0.1 A full scale
Light Source: Deuterium, tungsten
Detector: Photomultiplier
Zero Drift: 0.0004A/hour
Span Drift: 0
Scanning Speed: 100, 50, 20, and 5 nm/min

Monochromator:
Grating: 1200 lines/mm, blazed at 250 nm

Wavelength Range: Model 24, 340-700 nm, 190 nm optional
Model 25, 190-700 nm
Wavelength Accuracy: ±0.5 nm
Wavelength Repeatability: ±0.25 nm
Wavelength Scanning: 100, 50, 20, and 5 nm/min

Resolution: Model 24, 4 nm
Model 25, 0.2 nm
Dispersion: 2.7 nm/mm
Slit Width: Model 24, 2 nm
Stray Light: Model 24, <0.1% at 370 nm
Model 25, <0.1% at 220 nm

Operation

Calibration: Standard samples
Procedure: Manual provided
Training: Requires about 1 week
Unattended Period: Overnight
Maintenance: 21 sales and service centers in the U.S.

Requirements

Power: 115 Vac ±15 V, 50/60 Hz, 2 amps; 230 Vac ±30 V, 50/60 Hz, 2 amps
Weight: 31.75 kg (70 lbs)
Dimensions: 61 cm L, 40.6 cm D, 35.6 cm H (24" x 16" x 14")

Features

Model 24, fixed slit; Model 25, programmed slit
Output: Digital display, recorder output jack, printer

Options:		
Heated Sipper,	Model 24S	$4,250
	Model 25S	6,250
	Model 26S	6,450
Kinetics System	Model 24K	7,510
	Model 25K	9,510
	Model 26K	9,710

References

Manufacturer's Bulletin 7244-A

Cost

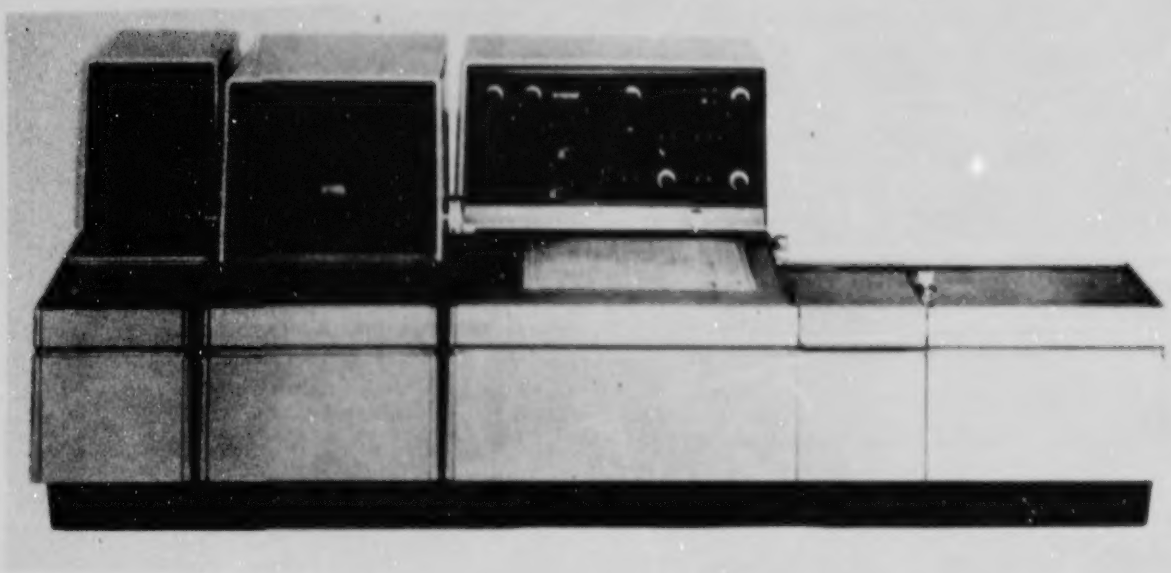
Model 24	$3,300
Model 25	$5,300
(Model 26)	($5,500)

Remarks

Address

Beckman Instruments, Inc.
Campus Drive & Jamboree Blvd.
Irvine, CA 92664
Attn: UV Product Line
(714) 833-0751

Ultraviolet/Visible Spectrophotometer
Beckman, ACTA Century Series



Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Single and double beam operation, ratio indicating, transmittance or absorption mode
Lower Detectable Limit	1 - 10 ppm
Range	Absorbance: 0 - 3 A Transmission: 0 - 200% T
Interferences	
Multiparameter Capability	
Sampling	Method: Automatic Volume: 40 ml Capacity: 10 samples/minute

Performance

Electronics: Solid state
Linearity:
Stability: 0.0005 A/hour
Accuracy: 0.003 A at 1.0 A; 0.010 A at 2.0A; 0.030 A at 3.0 A
Scale Expansion: 0.1A full scale
Detector: Photomultiplier
Zero Drift:
Span Drift: 0
Scanning speeds: 0.025, 0.1, 0.2, 0.5, 1.0, 2.0, and 4.0 nm/sec

Monochromator:
Grating: 1200 lines mm, blazed at 250 nm
Wavelength Range: 190-800 nm
Wavelength Accuracy: ± 0.1 nm
Wavelength Repeatability: 0.0015 A at 1.0 A; 0.005 A at 2.0 A; 0.015 A at 3.0 A
Resolution: <0.2 nm
Dispersion: 2.7 nm/min
Slit Width: Manual control, continuously variable from 0.005 to 7.0 mm
Stray Light: <0.1% at 370 nm

Operation

Calibration: Standard samples
Procedure: Manual available
Training: Requires about 2 weeks
Unattended Period: Overnight
Maintenance: 21 sales and service centers throughout the U.S.

Requirements

Power: 120 Vac ±10%, 50/60 Hz, 3.0 amps
Weight: 113 kg (250 lb)
Dimensions: 145 cm W, 53 cm H, 61 cm D (57" x 21" x 24")

Features

ACTA C111 includes recorder

Options:	Automatic Sampler	$3,840
	Total Reflectance, Accessory	$1,120
	Repetitive Scan	$ 445
	Sipper accessory, heated	$1,180
	Sipper accessory, unheated	$ 860

References

Manufacturer's Bulletin

Cost

ACTA C111	$9,710

Address

Beckman Instruments
Campus Drive & Jamboree Blvd.
Irvine, CA 92664
Attn: UV Product Line
(714) 833-0751

Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Double or single beam, double monochromator, ratio recording, automatic scanning, digital and recorder output.
Lower Detectable Limit	1 - 10 ppb
Range	% Transmission: 10, 20, 50, 100, 200, Var. Normal Absorbance: 0.1, 0.5, 1.0, 2.0, 3.0, concentration Expanded Absorbance: 0.01, 0.02, 0.05, 0.1, 0.2 Photometric Accuracy: 0.003 at 1.0 A; 0.01 at 2.0 A; 0.03 at 3.0 A
Interferences	
Multiparameter Capability	
Sampling	Method: Automatic Size: 14.6 cm, 22 cm, 17.8 cm Capacity: 10 samples/minute Temperature Compensation: Optional Pathlength: 10 cm
Performance	Electronics: Linearity: Stability: ±0.0005 A per hr or 0.005 A per day near zero absorbance Scale Expansion: .01 A full scale Light Source: Tungsten and deuterium; quartz iodine optional Detector: Photomultiplier and lead sulfide cell Zero Drift: Span Drift: 0 Monochromator: Gratings: One blazed at 250 nm (for UV-VIS) One blazed at 1200 nm (for NIR) Wavelength Range: 190-3000 nm Wavelength Accuracy: ±0.1 nm (190-800 nm) ±0.5 nm (800-3000 nm) } Model M-V11 Wavelength Repeatability Scanning Speeds: 190-800 nm; 4, 2, 1, 0.5, 0.25, 0.125, 0-0625, 0.03125 nm/sec 800-3000 nm; 16, 8, 4, 2, 1, 0.5, 0.25, 0.125 nm/sec Period Control: 0.5, 1, 2, 4, 8 sec Dispersion: Resolution: <0.05 nm (190-800 nm) <0.30 nm (800-3000 nm) Slit Width: Manual or programmed Stray Light: <0.001% 240 to 500 nm <0.001% 210 to 690 nm <0.01% at 2740 nm <0.1% at range limits
Operation	Calibration: Standard samples Procedure: Manual provided Training: Requires 2 weeks Unattended Period: Overnight Maintenance: 21 sales and service centers in the United States
Requirements	Power: 120 V ± 10%, 50/60 Hz, 3 amps Weight: 113 kg (250 lbs) Dimensions: 157 cm L, 61 cm D, 56 cm H (62" L, 24" D, 22" H)

Features

Output: Digital display, recorder, pushbutton operation, invalid command indicator, computer compatible (BCD, TTL & output), first derivative scanning, repetitive scanning

Options:	Sipper sampling accessory - heated	$1,180, unheated - $860
	Basic 4 x 1 automatic sampler	$6,100
	4 x 1 automatic sampler	$3,840
	Microcell holder kit	$ 200
	Dual wavelength accessory	$ 840

References

Manufacturer's Bulletin 7255

Cost

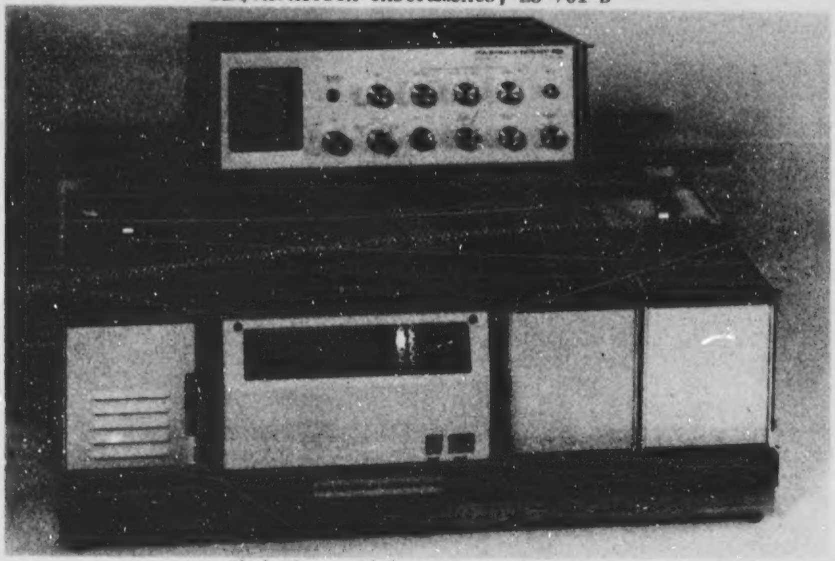
Model ACTA M-IV	$16,700
Model ACTA M-VI	$15,800
Model ACTA M-VII	$29,200

Address

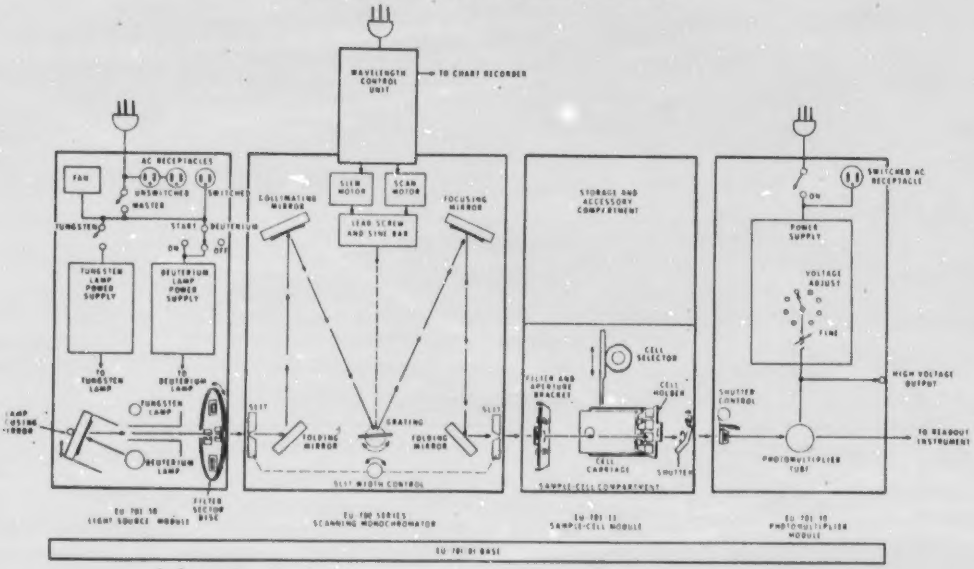
Beckman Instruments
Campus Drive & Jamboree Blvd.
Irvine, CA 92664

(714) 833-0751

Ultraviolet/Visible Spectrophotometer
GCA/McPherson Instruments, EU-701-D



Block Diagram Of The 701 Spectrophotometer

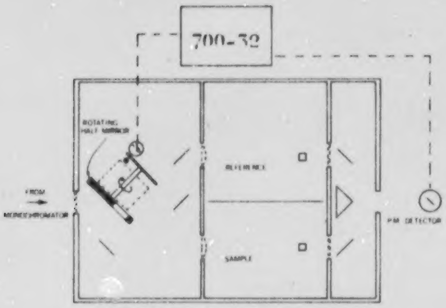

WAVELENGTH CONTROL UNIT
TO CHART RECORDER
AC RECEPTACLES
FAN
UNSWITCHED
SWITCHED
MASTER
TUNGSTEN
START
DEUTERIUM
ON
OFF
TUNGSTEN LAMP POWER SUPPLY
DEUTERIUM LAMP POWER SUPPLY
TO TUNGSTEN LAMP
TO DEUTERIUM LAMP
LAMP FOCUSING MIRROR
TUNGSTEN LAMP
DEUTERIUM LAMP
FILTER SECTOR DISC
EU 701 10 LIGHT SOURCE MODULE
SLEW MOTOR
SCAN MOTOR
LEAD SCREW AND SINE BAR
COLLIMATING MIRROR
FOCUSING MIRROR
SLIT
FOLDING MIRROR
GRATING
FOLDING MIRROR
SLIT
SLIT WIDTH CONTROL
EU 700 SERIES SCANNING MONOCHROMATOR
STORAGE AND ACCESSORY COMPARTMENT
CELL SELECTOR
FILTER AND APERTURE BRACKET
CELL HOLDER
CELL CARRIAGE
SHUTTER
SAMPLE-CELL COMPARTMENT
EU 701 11 SAMPLE-CELL MODULE
SWITCHED AC RECEPTACLE
ON
POWER SUPPLY
VOLTAGE ADJUST
FINE
HIGH VOLTAGE OUTPUT
SHUTTER CONTROL
PHOTOMULTIPLIER TUBE
TO READOUT INSTRUMENT
EU 701 10 PHOTOMULTIPLIER MODULE
EU 701 01 BASE

Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Single beam; digital readout
Lower Detectable Limit	

Range	ppb to percent
Interferences	
Multiparameter Capability	
Sampling	Method: Batch Volume: Capacity:
Performance	Electronics: 4 digit readout, BCD output Linearity: Stability: Scale Expansion: 0-0.1A, 0-0.5A, 0-1.0A, 0-2.0A, -0.3 - +0.7A; 0-10, 0-50,0-100%T Detector: IP28A Photomultiplier Zero Drift: ±0.001 A/hr Span Drift: Scanning Rates: Discrete sampling, signal averaging Monochromator: Czerny-Turner, 350mm, single pass Grating: 1180 lines/mm blazed at 250 nm 48 mm x 48 mm Wavelength Range: 185 to 750 nm 185 to 1,000 nm, optional Wavelength Accuracy: ±0.1 nm Wavelength Resettability: ±0.01 nm Resolution: 0.1 nm Dispersion: 2 nm/mm Slit Width: Manual, continuously variable between 2 and 2000 μ Stray Light: < 0.1% at 220 nm
Operation	Calibration: Standard samples Procedure: Training: Unattended Period: Maintenance:
Requirements	Power: 105 - 125 Vac, 50/60 Hz, 355 Watts (less readout modules) Weight: 64.5 kg (142 lb, less readout modules) Dimensions: 79 cm W, 49.5 cm D, 28 cm H (30.9" W, 19.5" D, 11" H, excluding control unit)
Features	Output: Recorder; digital display of photometric & wavelength data; direct reading of A, %T, I, Difference, Concentration, and dA/dt (Rate)
References	Manufacturer's Bulletin
Cost	Model EU-701-D $5,575
Address	GCA/McPherson Instrument 530 Main Street Acton, Massachusetts 01720 (617) 263-7733

H2O-MET
UV-Visible
GCA/McPherson 2
Sept. 1975

Ultraviolet/Visible Spectrophotometers
GCA/McPherson Instruments, EU-707


700-32
ROTATING HALF MIRROR
FROM MONOCHROMATOR
REFERENCE
SAMPLE
PM DETECTOR

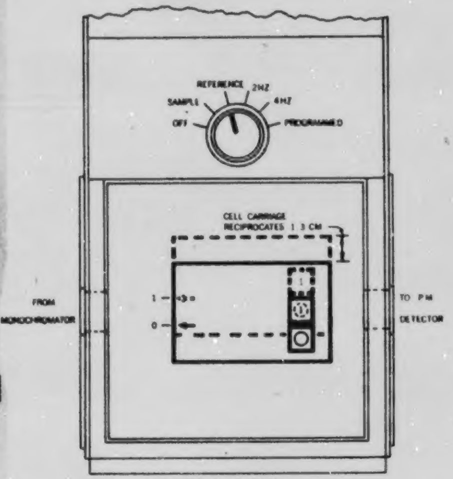
EU-707-11

Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Double beam, ratio-recording, rotating mirror, programmable mode, absorbance recording mode, digital readout.
Lower Detectable Limit	

Range	ppb to percent
Interferences	
Multiparameter Capability	
Sampling	Method: Batch Volume: Capacity:
Performance	Electronics: 4 digit readout, BCD output Linearity: Stability: Scale Expansion: 0-0.1A, 9-0.5A, 0-1.0A, 0-2.0A, -0.3 - +0.7A; 0-10, 0-50, 0-100%T Detector: IP28A Photomultiplier Zero Drift: < 0.001 Absorbance/hr Baseline Flatness: ±0.007A Scan Speeds: Discrete sampling, signal averaging. Monochromator: Czerny-Turner, 350 mm, eight automatically programmed filters Grating: 1180 g/mm blazed at 250 nm 48 x 48 mm Wavelength Range: 185 to 750 nm, standard 185 to 1000 nm, optional Wavelength Accuracy: ±0.1 nm Wavelength Resettability: ±0.01 nm Resolution: 0.1 nm Dispersion: 2 nm/mm Slit Width: Manually controlled, continuously variable between 5 and 2000 microns with 4 digit counter Stray Light: <0.1% at 220 nm
Operation	Calibration: Procedure: Training: Unattended Period: Maintenance:
Requirements	Power: 105-125 Vac, 50/60 Hz, 380 Watts (less readout module) Weight: 79 kg (174 lb, less readout module) Dimensions: 79 cm W, 53 cm D, 28 cm H (30.9" W, 21" D, 11" H, excluding control unit)
Features	Output: mv Recorder; digital display of photometric and wavelength data; direct reading of A, %T, Concentration, I, Difference, and dA/dt (Rate)
References	Manufacturer's Bulletin
Cost	Model EU-707-D $7,425
Address	GCA/McPherson Instrument 530 Main Street Acton, Massachusetts 01720 (617) 263-7733

Ultraviolet/Visible Spectrophotometers

GCA/McPherson Instruments EU-721-D


REFERENCE
2HZ
SAMPLE
4HZ
OFF
PROGRAMMED
CELL CARRIAGE
RECIPROCATES 1 3 CM
FROM
MONOCHROMATOR
1
0
TO PM
DETECTOR

TOP VIEW OF 721 11
ALTERNATING CELL MODULE

Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Single beam, ratio-recording, programmed alternate positioning of reference and sample cells in a fixed light path, programmable mode, digital readout.
Lower Detectable Limit	
Range	ppb to percent
Interferences	
Multiparameter Capability	
Sampling	Method: Batch and Automatic Volume: ml Capacity: samples/minute

Performance

Electronics: 4 digit readout, BCD output
Linearity:
Stability:
Scale Expansion: 0-0.1A, 0-0.5A, 0-1.0A, 0-2.0A, -0.3-+0.7A; 0-10, 0-50, 0-100%T
Detector: 1P28A Photomultiplier
Zero Drift: <0.001 Absorbance/hr
Baseline Flatness: <0.001 Absorbance from 185 to 850 nm with appropriate PM tube
Scan Speeds: Discrete sampling, signal averaging

Monochromator: Czerny-Turner, 350 mm eight automatically programmed filters
Grating: 1180 g/mm blazed at 250 nm 48 x 48 mm
Wavelength Range: 185 to 750 nm, standard
185 to 1000 nm, optional
Wavelength Accuracy: ±0.1 nm
Wavelength Resettability: ±0.01 nm
Resolution: 0.1 nm
Dispersion: 2 nm/mm
Slit Width: Manually controlled, continuously variable between 5 and 2000 microns with 4-digit counter
Stray Light: <0.1% at 220 nm

Operation

Calibration:
Procedure:
Training:
Unattended Period:
Maintenance:

Requirements

Power: 105-125 VAC, 50/60 Hz, 357 watts (less readout module)
Weight: 70 kg (154 lbs, less readout modules)
Dimensions: 79 cm W, 53 cm D, 28 cm H (30.9" x 21" x 11", excluding control unit)

Features

Output: Recorder; digital display of photometric & wavelength data; direct reading of A, %T, Concentration, Difference, and dA/dt (Rate).

References

Manufacturer's Bulletin

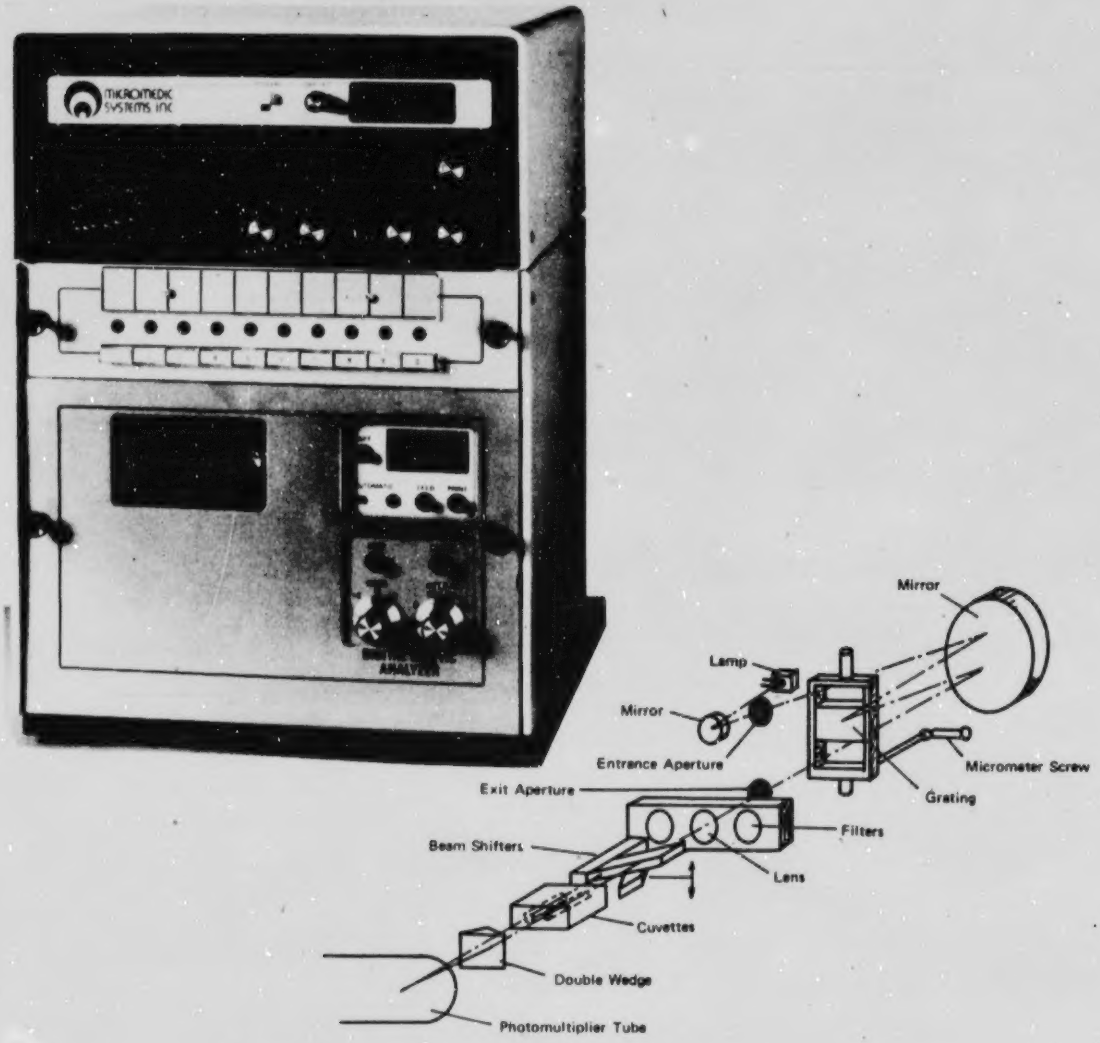
Cost

Model EU 721-D $6,250

Address

GCA/McPherson Instrument
530 Main Street
Acton, Massachusetts, 01720
(617) 263-7733

Ultraviolet/Visible Spectrophotometer
Micromedic MS-2

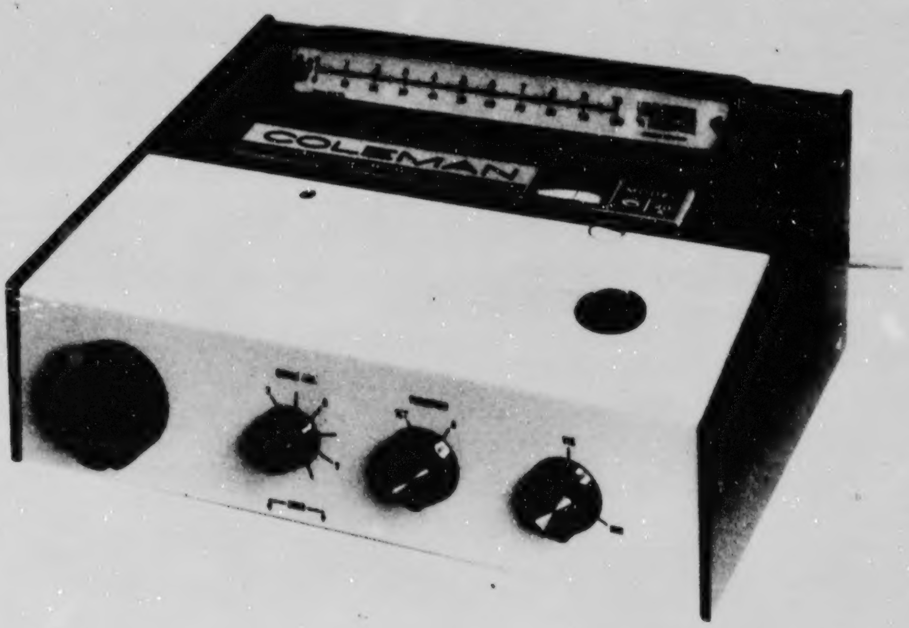

MIKROMEDIC SYSTEMS INC
ANALYZER
Mirror
Lamp
Mirror
Entrance Aperture
Micrometer Screw
Exit Aperture
Grating
Filters
Beam Shifters
Lens
Cuvettes
Double Wedge
Photomultiplier Tube

Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Single beam, two 17 μl cuvettes, pressure sample feed, digital and printer output
Lower Detectable Limit	

Range	ppb to percent for environmental samples	
Interferences		
Multiparameter Capability		
Sampling	Method: Batch Volume: ml Capacity: samples/minute	
Performance	Electronics: Solid state, LED readout, regulated power supplies Linearity: <1% Stability: 0.001 A per day Scale Expansion: Detector: Photomultiplier Zero Drift: 0.001 A per day Repeatability: ±0.001 A Span Drift:	
	Monochromator: Diffraction grating Grating: 590 lines per mm blazed at 350 nm Wavelength Range: 200 to 700 nm Optional up to nm Wavelength accuracy: ±1 nm Wavelength repeatability: 0.3 nm Resolution: 0.0003A Dispersion: Slit Width: 8 nm Stray Light: <1% at 200 nm	
Operation	Calibration: Standard samples Procedure: Defined in manual Training: At installation Unattended Period: Maintenance: Warranty, one year, service kits	
Requirements	Power: 115 ±10% Vac, 60 Hz, 625 VA 230 ±10% Vac, 50 Hz, optional Weight: Sampling and optics; 22 kg (47 lb) Electronics module, 22 kg (47 lb) Dimensions: Sampling and optics: 45 cm H, 32 cm W, 43 cm D (17.5" x 12.5" x 17") Electronics Module: 45 cm H, 32 cm W, 33 cm D (17.5" x 12.5" x 13")	
Features	Output: Digital display and printer	
	Options: BCD output	$
	UV attachment	$ 625
	Printer	$1,595
	Dedicated test channel package (10 channels)	$1,495
	Enzyme option	$3,690
	Temperature Controller	$ 775
References	Manufacturer's Bulletin	
Cost	Model MS-2	$5,795
Address	Micromedic Systems, Inc. 102 Witmer Rd Horsham, PA 19044 (215) 674-8500	

Ultraviolet/Visible Spectrophotometer

Perkin-Elmer Coleman Junior Series



Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Single beam, linear absorbance and snap-in scales that can be calibrated for direct concentration readout.
Lower Detectable Limit	

Range

Interferences

Multiparameter Capability

Sampling

Method: Batch
Volume: 0.007 ml to 12.0 ml
Temperature Control:
Path Length:

Performance

Electronics: Solid state
Linearity:
Stability:
Scale Expansion:
Light Source: Tungsten
Detector: Photomultiplier
Zero Drift:
Span Drift:

Monochromator:
Grating:
Wavelength Range: 325-825 nm
Wavelength Accuracy: ±1 nm at 610 nm
Wavelength Repeatability:
Resolution: 20 nm
Dispersion:
Slit Width:
Stray Light:

Operation

Calibration: Standard samples
Procedure: Clinical methods manual available
Training:
Unattended Period:
Maintenance: Service centers in the U.S.

Requirements

Power: 115 V AC, 50/60 Hz
Weight: 15 kg (33 lbs)
Dimensions: 40.5 cm W, 38 cm D, 20 cm H
(16 in. W, 15 in. D, 8 in. H)

Features

Output: Analog Meter; 0- mv Recorder; Digital Display
Options:

Digital Printer, Model S6	$1,832
Flame Photometer, Model 21	947
Photo Fluorometer, Model 12C	846
Vacuvette Accessories	153

References

Manufacturer's Bulletin

Cost

Junior	Model	6A	(6006)	$ 638
"	"	6C	(6016)	674
"	"	II	(6034)	852
"	"	IIA	(6036)	852

Address

Perkin-Elmer
Coleman Division
2000 York Rd.
Oakbrook, Illinois 60521
(312) 887-0770/ 242-4050

Ultraviolet/Visible Spectrophotometer
Perkin-Elmer, Coleman Model 54

Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Single beam. Digital readout.
Lower Detectable Limit	

Range

Absorbance: 0-2A, linear, ±0.001A at 1A
Transmittance: 0-100% T
Concentration: 0-1999

Interferences

Multiparameter Capability

Sampling

Method: Batch or semi-automatic (up to 95 samples)
Volume: ml
Capacity: samples/minute
Temperature Control: ±0.1°C from 25° to 40°C
Sample Temperature: ±0.5°C of water bath temperature
Pathlength: 10 mm

Performance

Electronics:
Photometric Linearity: <0.5% T
Photometric Repeatability: ±0.5% T
Stability: 0.002A/per hour at 0A
Scale Expansion:
Light Source:
Detector: Photomultiplier
Zero Drift:
Span Drift:

Monochromator:
Grating:
Wavelength Range: 330-835 nm
Wavelength Accuracy: ±1 nm
Wavelength Resolution: ±1 nm
Spectral Bandwidth: 20 nm
Resolution:
Dispersion:
Slit Width:
Stray Light: <0.3% at 340 nm

Operation

Calibration: Standard samples
Procedure: Notes available
Training: Requires about hours
Unattended Period: Up to minute
Maintenance: service centers in U.S.

Requirements

Power: 115 V AC, 50/60 Hz
Weight:
Dimensions:

Features

Output: 3.5 digit display, recorder connections, digital BCD, (b2,4,8), TTL

Options:		
	Automatic sampler, model 48	$1,886
	Digital printer, model 47BCD	1,832
	Chart recorder, model 56	1,584
	System controller	947
	Enzyme calculator	1,577
	Print timer	442

References

Manufacturer's Bulletin

Cost

Model 54	$1,894

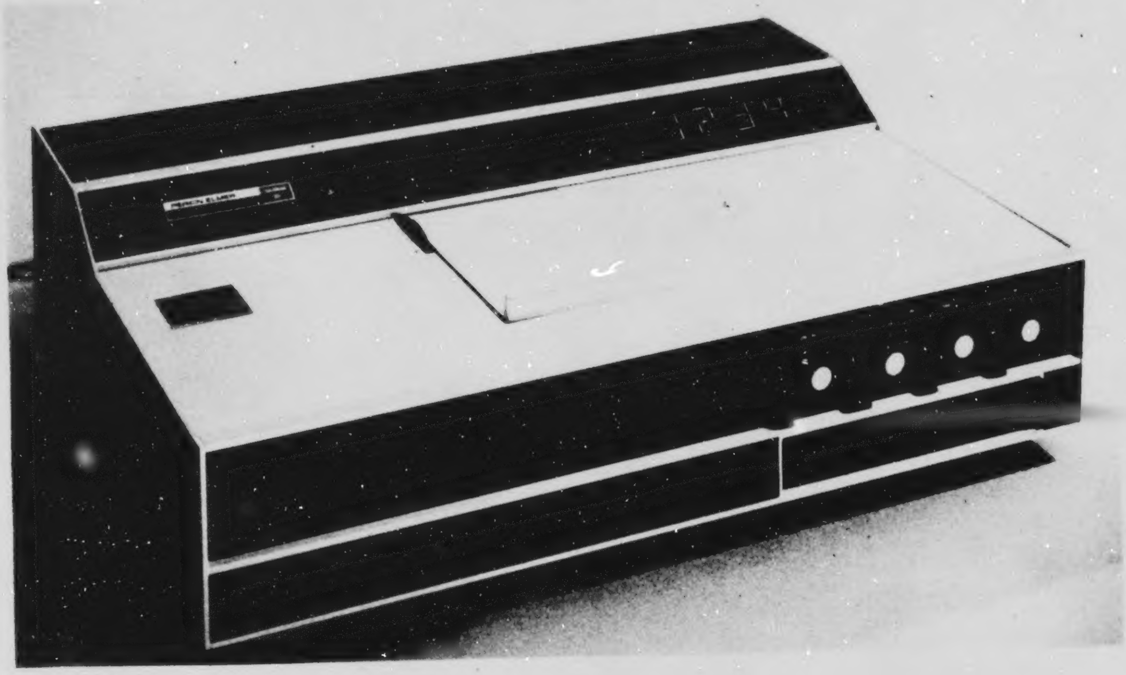
Address

Perkin Elmer
Coleman Division
2000 York Rd.
Oakbrook, Illinois 60571
(312) 887-0770/242-4050

H20-MET
UV-Visible
Perkin-Elmer 3
Sept. 1975

Ultraviolet/Visible Spectrophotometer

Perkin-Elmer Coleman Model 55



Class	Laboratory
Categories:	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Single beam, digital readout
Lower Detectable Limit	Depends on path length and consistency of solution

Range

Absorbance: 0-3 A, ±0.5 A
Transmittance: 0-100% T, 0-200% T, ±0.3% T
Concentration: 0.1 to 10X

Interferences

Multiparameter Capability

Sampling

Method: Batch and semiautomatic
Volume: 2-4 ml
Capacity: 2 samples/minute
Temperature Control: 25, 30, 32, and 37°C
Path Length: 20, 50 or 100 mm

Performance

Electronics: Solid state
Linearity: 0.2% T per 8 hours
Stability: <0.005 A per 8 hours
Light Source: Quartz iodine
Detector: Photomultiplier
Zero Drift:
Span Drift:

Monochromator: Littrow type
Grating: x mm
Wavelength Range: 325-800 nm, 200 nm optional
Wavelength Accuracy: ±1 nm
Wavelength Repeatability: ±0.2 nm
Resolution: 2 nm
Dispersion:
Slit Width:
Stray Light: <0.1% at 340 nm

Operation

Calibration: Standard samples
Procedure:
Training:
Unattended Period:
Maintenance: Service centers in the U.S.

Requirements

Power: 115 Vac +15%-10%, 60 Hz, Watts
230 Vac +15%-10%, 50 Hz, Watts
Weight: 25 kg (55 lbs)
Dimensions: 58.4 cm W, 41.9 cm D, 17.1 cm H
(23 in. W, 16.5 in. D, 6.75 in. H)

Features

Output: Four digit readout, recorder output, BCD

Options:	
UV Accessory, Model 204	$ 620
Automatic Sampler, Model 200	693
Digital Printer, Model 5-050	1,832
Chart Recorder Model 56	1,584
Enzyme Calculator	1,577
Print Timer	442
System Controller	947
Sample Programmer, Model 48	1,722
Microflow Cells	

References

Manufacturer's Bulletin

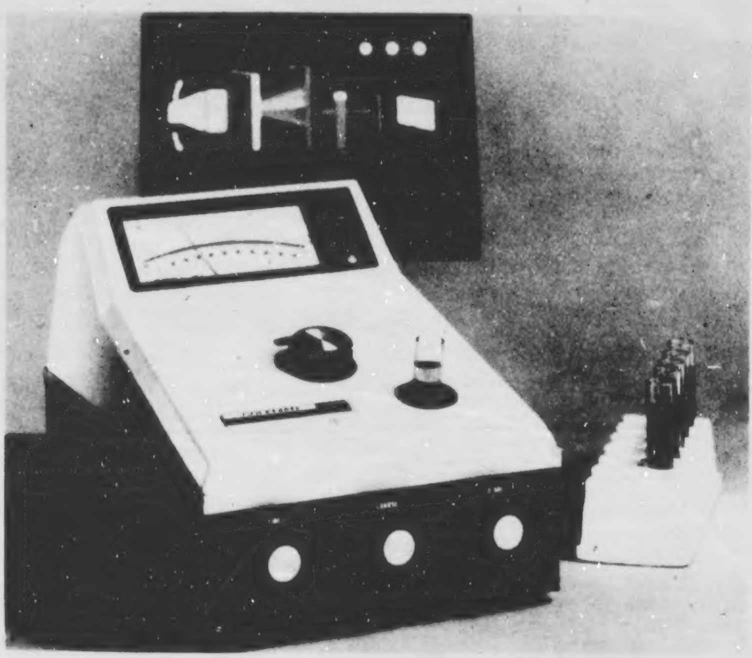
Cost

Model 55 $3,219

Address

Perkin-Elmer
Coleman Instruments Division
2000 York Road
Oak Brook, IL 60521
(312) 887-0770 /242-4050

Ultraviolet/Visible Spectrophotometer
Perkin Elmer, Coleman Model 295

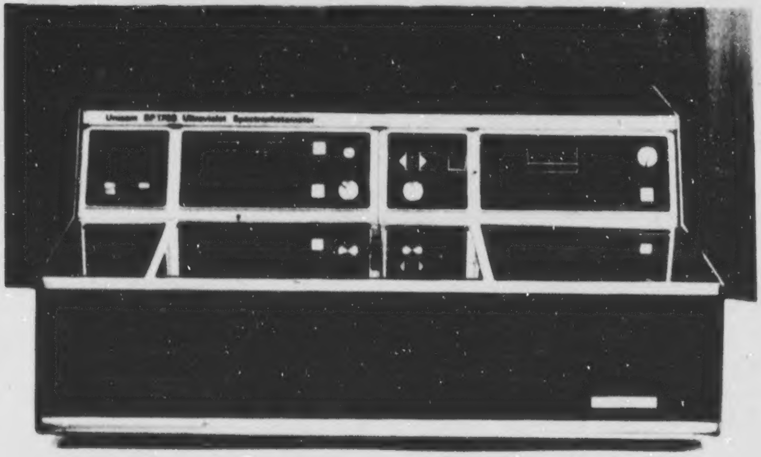


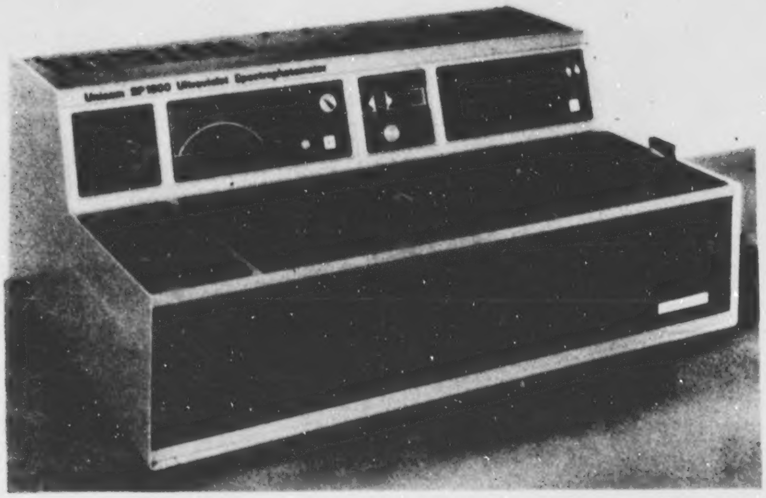
Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Single beam, single lamp, single monochromator, analog meter readout
Lower Detectable Limit	

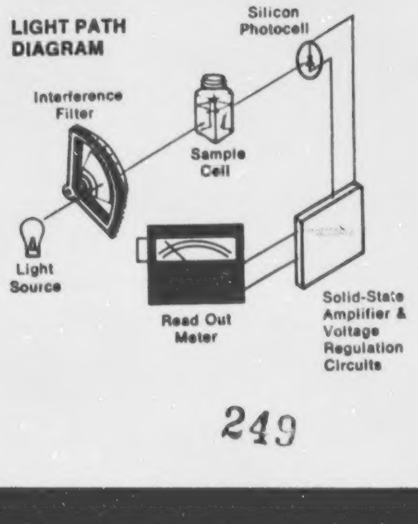
Range	Absorbance: 0-2.0 A Transmittance: 0-100% T, ±0.5% T	
Interferences		
Multiparameter Capability		
Sampling	Method: Batch Volume: 0.007 ml to 12.0 ml Capacity: samples/minute Temperature Control: None Pathlength:	
Performance	Electronics: Solid state Linearity: Stability: Scale Expansion: Light Source: Tungsten Detector: Phototube Zero Drift: Span Drift: Monochromator: Echelette Grating: Wavelength Range: 400-700 nm Wavelength Accuracy: ±1 nm at 610 nm Wavelength Repeatability: ±0.5 nm Wavelength Scanning: Resolution: Dispersion: Slit Width: Stray Light:	
Operation	Calibration: Standard samples Procedure: Manual provided Training: Teaching package, aids, and wall charts available Unattended Period: None Maintenance: 33 service centers in the U.S.	
Requirements	Power: Weight: 7.7 kg (17 lbs) Dimensions: 25.4 cm W, 42 cm D, 23.4 cm H (10" W, 16.5" D, 9.25" H)	
Features	Output: Analog meter Options: Educational aids Accessories and supplies	
References	Manufacturer's Bulletin	
Cost	Model 295	$437.
Address	Perkin Elmer Coleman Instrument Division 2000 York Rd. Oakbrook, Illinois 60521 (312) 887-0770/242-4050 Attn:	

Ultraviolet/Visible Spectrophotometer

Pye-Unicam Models 1700, 1800


Unicam SP1700 Ultraviolet Spectrophotometer


Unicam SP1800 Ultraviolet Spectrophotometer


LIGHT PATH DIAGRAM
Silicon Photocell
Interference Filter
Sample Cell
Light Source
Read Out Meter
Solid-State Amplifier & Voltage Regulation Circuits

Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Double beam, chopper modulated ratio measurement, meter or digital readout
Lower Detectable Limit	
Range	Absorbance: 0-0.2, 0.5, 1, 2, linear, ±1% of absorbance reading or 0.002 A, whichever is the greater, continuously variable over range -0.1 to +2 A
Interferences	
Multiparameter Capability	
Sampling	Method: Batch or automatic Volume: 8.0 ml Capacity: 1.33 samples/minute Temperature Control: Ducts provided
Performance	Electronics: Solid state Linearity: 0.001 A Stability: 0.0005 A Scale Expansion: Recorder 0.05 A full scale, SP1700 10x Light Source: Tungsten and deuterium lamps Detector: EMI 9634QB photomultiplier, standard EMI 9558BQ photomultiplier, optional Zero Drift: Span Drift: 0.0005 A/hr Monochromator: Ebert f/10 Grating: 1276 lines/mm Wavelength Range: 190-700 nm, 850 nm optional Wavelength Accuracy: ±0.5 nm Wavelength Resettability: 0.5 nm Bandpass: 3 nm per mm slitwidth Resolution: 0.1 nm Dispersion: 3 nm/mm Slit Width: Continuously variable from 0.01 to 1.0 mm Stray Light: < 1% at 200 nm
Operation	Calibration: Standard samples Procedure: Manual available Training: Unattended Period: Indefinite Maintenance: Service centers in U.S.
Requirements	Power: 110-120 Vac, ±10% 50 or 60 Hz, 200 VA 200-250 Vac, 50 or 60 Hz, 200 VA Weight: 70 kg (154 lb) Dimensions: 78.6 cm L, 55.4 cm H, 33.2 cm D (31" L, 21.8" H, 31.1" D)

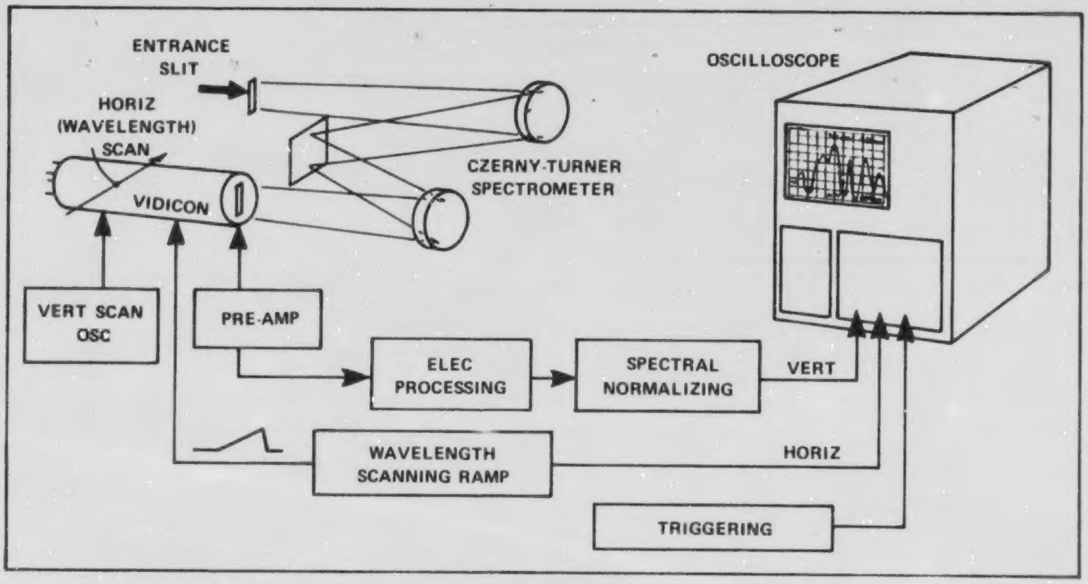
Features	Output: Analog meter; recorder and printer output, BCD output	
	Options: Automatic sampler, Model SP40, 50 sample	$1,825
	Digital printer, Model DR16	2,200
	Fluorescence, Model SP860	1,020
	Reflectance, Model SP890	1,050
	Wavelength selector, Model SP1803	2,100
	Program controller, Model SP1805	2,035
	Densitometer, Model SP1809	2,365
References	Manufacturer's Bulletin	
Cost	Model SP 1700, digital readout	$9,410
	Model SP 1800	$8,410

Address

Pye Unicam
750 S. Fulton
Mt. Vernon, NY 10550
(914) 664-4500
Attn: G. Ciancanelli

Ultraviolet/Visible/Near IR Spectrometer

Tektronix, Rapid Scan Spectrometer


ENTRANCE SLIT
OSCILLOSCOPE
HORIZ (WAVELENGTH) SCAN
CZERNY-TURNER SPECTROMETER
VIDICON
VERT SCAN OSC
PRE-AMP
ELEC PROCESSING
SPECTRAL NORMALIZING
VERT
WAVELENGTH SCANNING RAMP
HORIZ
TRIGGERING

Class	Laboratory or mobile
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	The RSS receives light, disperses it with a Czerny-Turner grating monochromator and images the spectrum on a specially-designed silicon-vidicon. The spectrum is recorded at all wavelengths simultaneously on the vidicon detector. An electron beam scans the detector in four milliseconds and the spectrum then appears on the display screen of the oscilloscope.
Lower Detectable Limit	The noise-equivalent power (NEP) represents the smallest detectable signal with a signal/noise ratio of 1. The RSS has an NEP of 20 pW/nm with the low-dispersion grating and 200 pW/nm with the high-dispersion grating.
Sampling	The sample for the RSS is any source of radiation between 250 and 1100 nm wavelength. Since such radiation could be light reflected from foliage, water, etc., or the light transmitted by a medium, the sample size cannot be meaningfully specified. Since these sources of radiant power may change with time, the instrument can sample the spectrum as fast as 250 times per second. As the spectrometer and detector are remote from the source, temperature compensation is not required.
Performance	Electronics: System Linearity: 1% or better Dark current variation compensated for Detector: Silicon vidicon detector, quartz face plate Light Source: Ambient or user supplied Monochromator: Czerny-Turner Grating: 47 x 41 mm, 150 lines per mm blazed at ≈ 500 nm 47 x 41 mm, 1200 lines per mm Wavelength Range: 250-1100 nm Wavelength Accuracy: ±10 nm (150 l/mm), ±3 nm (1200 l/mm) Wavelength Repeatability: ±1 nm (150 l/mm), ±0.5 (1200 l/mm) Scanning Speed: 4 to 20 ms Resolution: 4 nm (150 l/mm), 0.4 nm (1200 l/mm) Dispersion: 32 nm/mm (150 l/mm), 3.2 nm/mm (1200 l/mm) Slit Width: 10, 20, 50, 100, 200, 500, 1000 μm Stray Light: <1% @ 600 nm
Operation	Calibration: Standard lamps (done at factory) Procedure: Covered in operator's manual Training: Required about 4 hours Maintenance: 32 service centers in U.S. for electronics, factory service for optics
Requirements	Power: Derived from any Tektronix 7000-Series oscilloscopes (e.g., 7313), pulls about 30 watts Weight: 9.5 kg (21 lb), spectrometer and plug-in Dimensions: 30 cm L, 17 cm W, 18 cm H (12" L, 6.65" W, 7" H)

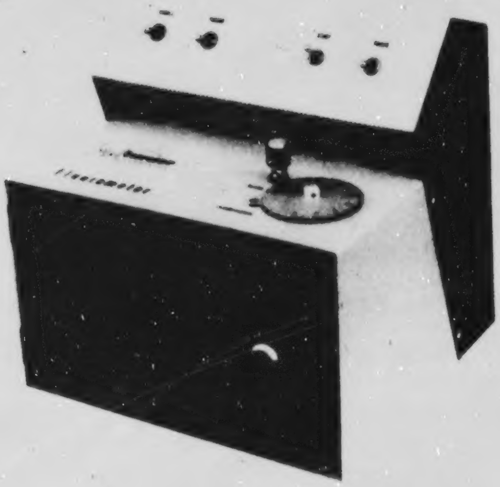
Features	Output: Analog voltage or CRT display	
	Options: With or without spectroradiometric calibration	
	Polaroid camera readout	$400-$1,000
	Spectroradiometric calibration	$1,160
References	Manufacturer's Bulletin #A-2582	
Cost	Model 7J20	$12,600

Address

Tektronix
P.O. Box 500
Beaverton, Oregon 97005
Attn: Jim Nicholson
or Jere Marrs 48-188
(503) 644-0161 , X-6654

Filter Fluorometer

Turner, Models 110, 111



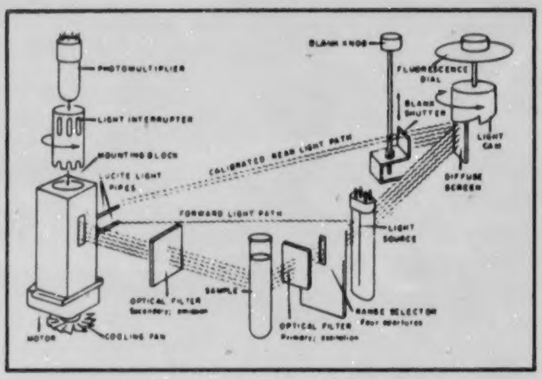

PHOTOMULTIPLIER
LIGHT INTERRUPTER
MOUNTING BLOCK
LUCITE LIGHT PIPES
CALIBRATED BEAM LIGHT PATH
BLANK KNOB
FLUORESCENCE DIAL
BLANK SHUTTER
LIGHT CAM
DIFFUSE SCREEN
FORWARD LIGHT PATH
LIGHT SOURCE
OPTICAL FILTER Secondary; emission
SAMPLE
RANGE SELECTOR Four apertures
OPTICAL FILTER Primary; excitation
MOTOR
COOLING FAN

Diagram of Turner Double Beam Filter Fluorometer

Class	Laboratory or mobile
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Double beam, ratio measurement, colored light filters are used to optically select the fluorescent emission of light from a sample of unknown concentration.
Lower Detectable Limit	Cadmium: 1 ppm (Ryan et al., Anal. Chim. Acta 34, 491 (1966)) Lead: Screening by erythrocyte protoporphyrin monitoring in blood
Range	Cd: 1 ppb - 0.25 ppm
Interferences	Zn is positive interference
Multiparameter Capability	General purpose laboratory instrument, capable of determining many cations, anions and other substances, e.g., chlorophyl, dyes, H_2S, beryllium, selenium
Sampling	Method: Discrete and continuous flow sampling Volume: 0.25 ml with high sensitivity accessory Capacity: Dependent on method Temperature Compensation: Available as accessory from external water bath

Performance

Electronics:

Linearity: ±1% of full scale
Stability: ±1% of full scale
Scale Expansion: 1x, 3x, 10x, 30x, plus 10x with sensitivity accessory
Detector: Photomultiplier, S4 response
Zero Drift:
Span Drift:
Wavelength Range: 254 to 600 nm

Operation

Calibration: Standard solutions
Procedure: Blank, read sample, determine concentration from curve
Training: Operations and maintenance manual provided
Unattended Period:
Maintenance: Minimal

Requirements

Power: 105 - 130 Vac, 1.3 amps, 60 Hz; options: 50 Hz, mobile
Weight: 17.7 kg (39 lb)
Dimensions: 29 cm D, 30 cm W, 33 cm H (11.5" D, 12" W, 13" H)

Features

Output: Model 111, automatic servo dial; recorder output Model 110 has null meter manual control for optical bridge, no recorder output

Options:

Recorder	$439
Continuous Flow Accessories	$Varies with type @$250
TLC Scanner	$995
Uranium Assay Accessory	$120.60

References

Manufacturer's Bulletin

Cost

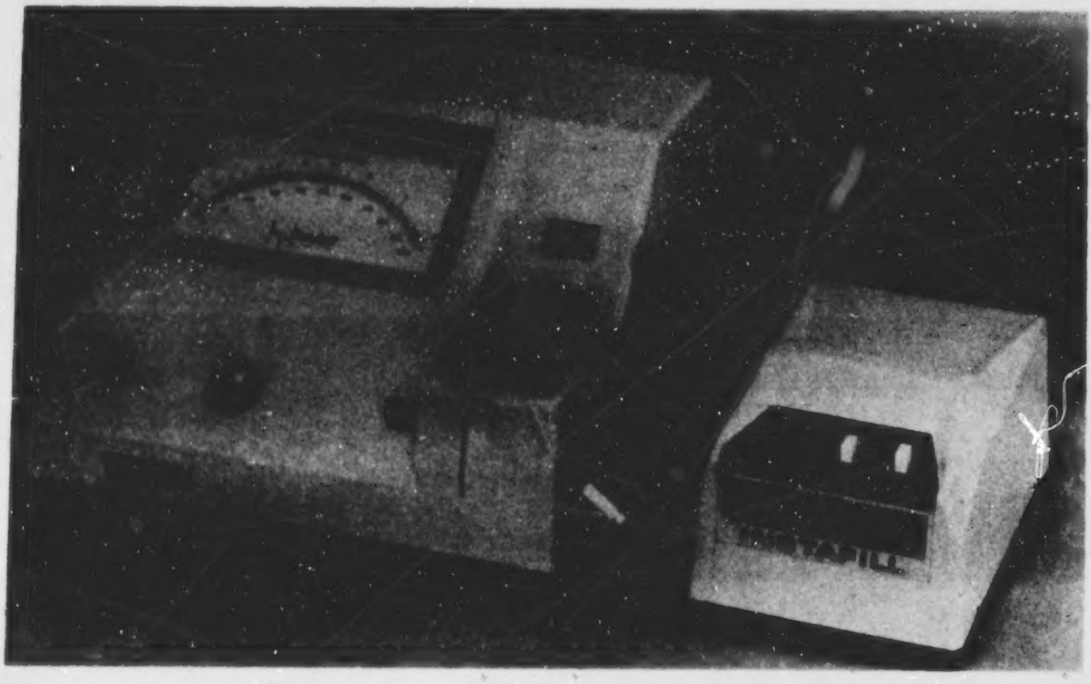
Model 110	$1,295
Model 111	$1,820

Address

Turner Associates, Division American Sterilizer Company
2524 Pulgas Avenue
Palo Alto, CA 94303
(415) 324-0077

Ultraviolet/Visible Spectrophotometer

Turner Models 330 and 350



Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood Tissue, Serum, Urine
Principle of Operation	Single beam. Meter readout.
Lower Detectable Limit	Mercury: 2 μg without concentration (Nabrzyskim, Anal. Chem. 45, 2438 (1973)) Cadmium: 0.006 to 0.008 μg/ml (Ackerman et al., Anal. Chem. 250, 353 (1970))
Range	ppb to %, depends on the particular analysis 0 - 100% Transmission 0 - 2 Absorbance
Interferences	Dirty or scratched cells
Multiparameter Capability	Far UV extension to 210 nm, infrared accessory to 1000 nm
Sampling	Method: Discrete, flow-through, continuous Volume: Depends on cuvet size or attachment used. With 100 mm x 13 mm cuvets, minimum volume is approximately 4 ml. With the INSTAFILL accessory sample size down to 0.55 ml with 0.075 ml in the cell. Temperature Control: Water jacket provided, requires an external temperature regulated water supply and pump.

Performance

Electronics:

Linearity: 1.0%
Stability: Less than 1% change per hour after warmup
Scale Expansion:
Detector: Photodiode (210-710 nm range)
Meter Accuracy: ±1% with Model 330; 0.5% with Model 350

Monochromator:

Grating: Ebert mounting, f7 · 590 lines/mm
Stray Light: < 0.5% throughout operating range
Wavelength Range: 335-710 nm (standard)
Bandwidth: 9 nm (resolution)
Accuracy of Wavelength Setting: ±2 nm throughout wavelength range
Dispersion:
Slit Width: 0.79 mm

Operation

Calibration: Standard solutions
Procedure: Calibration curve; standard additions;
Training: Manual provided
Unattended Period:
Maintenance: Service available from distributors or Turner factory. Technician can repair from manual

Requirements

Power: 100-130 or 200-260 Vac; 50-60 Hz; 30 W average, 50 W maximum
Weight: 6.3 kg (14 lb)
Dimensions: 29 cm W x 30.5 cm D x 16 cm H
(11-3/4 " x 12" x 6-1/2 ")

Features

Output: Model 330 -- 10.2 cm (4") analog meter
Model 350 -- 17.8 cm (7") analog meter
Recorder output for 0-1V or 0-1 ma

Options:

Cuvet Holders; Round, Jacketed, Square, Vacuum Emptying	$Varies
Ultraviolet Attachment, to 215 nm	$995.00
Instafill Automatic Filling Device	$695.00
IR Accessory	$ 43.95

Wavelength Setting: By means of digital counter

References

a) Manufacturer's Bulletin, "Turner Laboratory Instruments," 1972
b) Instafill Brochure

Cost

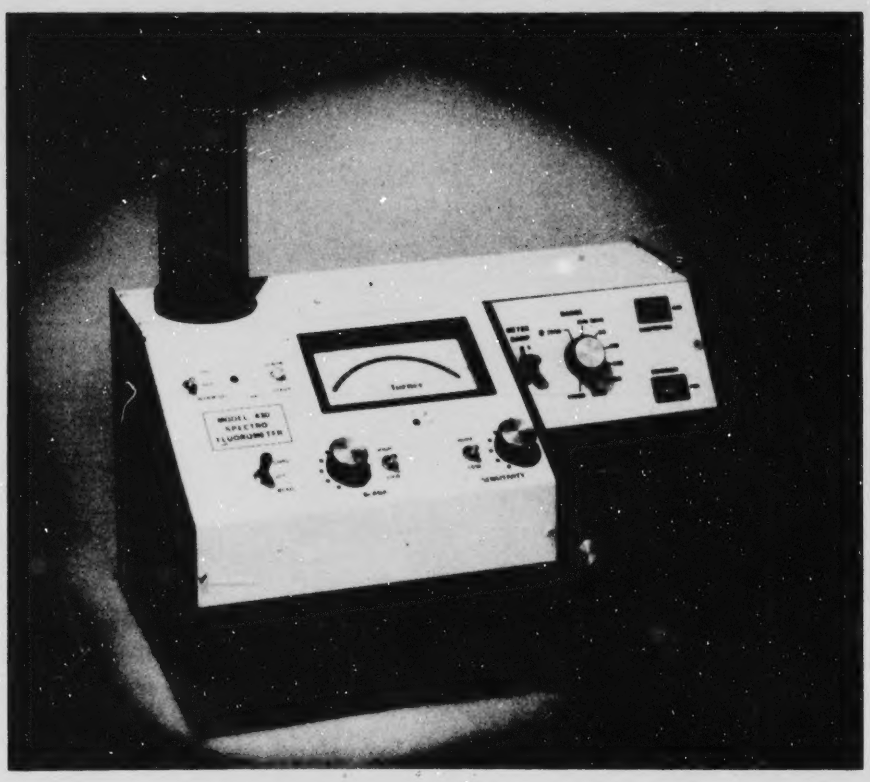
Model 330	$645
Model 350	795

Address

Turner Associates, Division American Sterilizer Company
2524 Pulgas Avenue
Palo Alto, CA 94303
(415) 324-0077

Spectrofluorometer

Turner, Model 430



Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Double beam, ratio measurement, dual monochromaters for excitation/emission wavelength with 150 watt xenon lamp.
Lower Detectable Limit	Cadmium: 1 ppb (Ryan, et al., Anal. Chem Acta 34, 491 (1966)) Lead: Screening by erythrocyte protoporphyrin monitoring in blood (info. from Turner) Mercury: 10 ng/ml (Holzbelaer et al., Anal. Chim. Acta 64, 333 (1973))
Range	Cd: 1 ppb - 0.25 ppm Hg: 10 - 500 ng/ml
Interferences	Cd: Znis positive Hg: Cyonide, EDTA, iodide, sulfide
Multiparameter Capability	
Sampling	Method: Batch and automated adapter Minimum Volume: 2.2 ml in square cuvet 1.8 ml in round cuvet Capacity: Dependent on method Temperature Control: ±1°C of external water bath temperature with built-in water jacket

Performance

Electronics: Solid state

Linearity:
Stability:
Scale Expansion: 1000x
Detector: Photomultiplier
Zero Drift:
Span Drift:
Wavelength Range: Excitation, 200 to 1000 nm
Emission, 300 to 700 nm
Optical Emission, 200 to 750 nm
Bandwidth: Excitation, 15 nm
Emission, 15 to 60 nm

Operation

Calibration: Standard solutions
Procedure: Direct concentration from standards, auto blank suppression
Training: Manual provided
Unattended Period:
Maintenance: Minimal, available from distributors or manufacturer

Requirements

Power: 105 to 130 Vac, 48 to 65 Hz, 340 W; optional: 210-260 Vac
Weight: 40 kg (89 lb)
Dimensions: Electro optical unit 53 cm W, 30 cm D, 28 cm H
(21"W, 11.75" D, 11" H) exclusive of lamp chimney
Xenon lamp power supply 22 cm W, 40 cm D, 23.5 cm H
(8.75" W, 16" D, 9.25" H)

Features

Output: Analog meter

Options:	
Motorized wavelength drive	$398
Automated chemistry adapter	$297
Multiposition sample compartment	$Varies
Polarization attachment	$Varies

References

Manufacturer's Bulletin

Cost

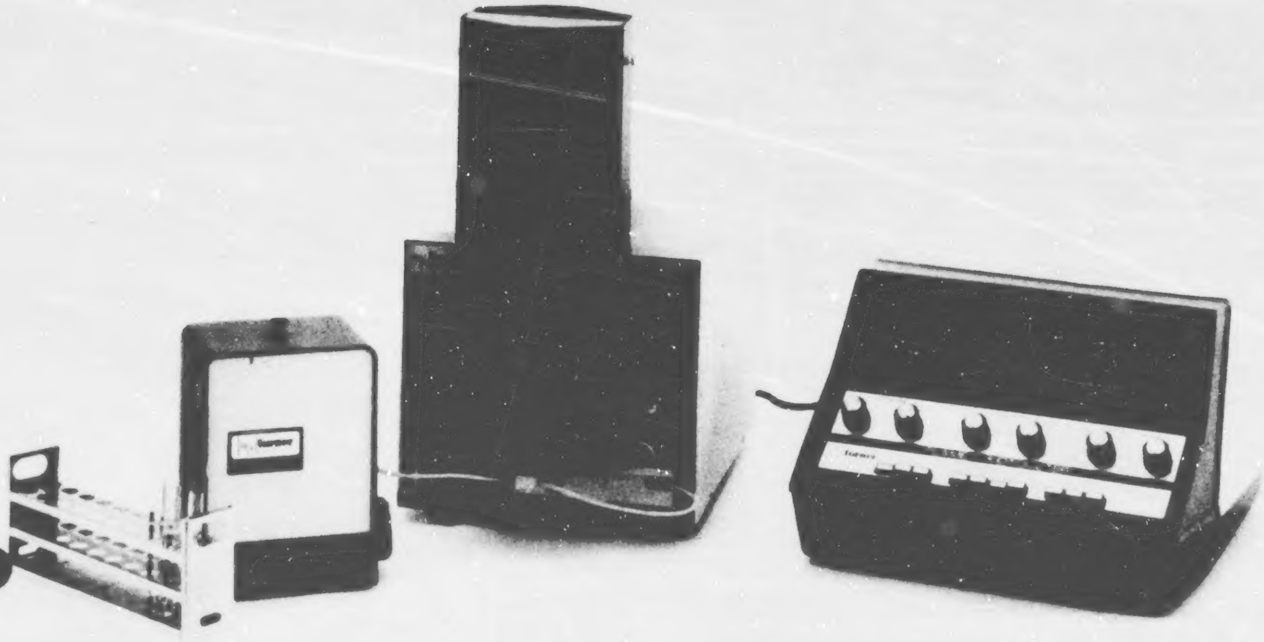
Model 430 $4,185

Address

Turner Associates, Division American Sterilizer Company
2524 Pulgas Avenue
Palo Alto, CA 94303
(415) 324-0077

Flame Photometer

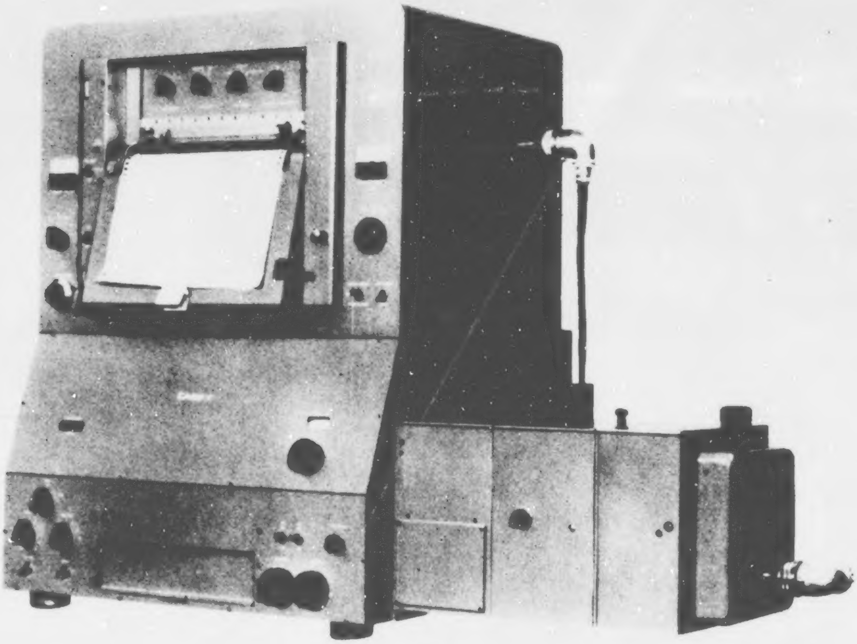
Turner, Model 510

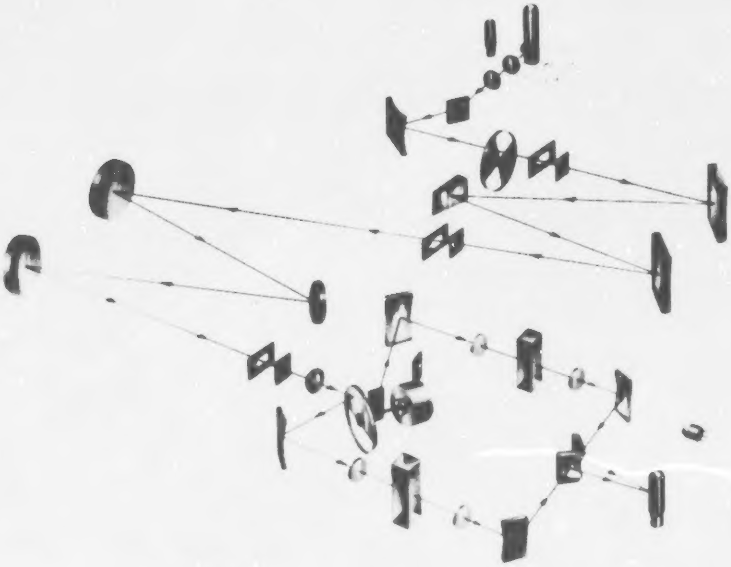


Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Emission photometer designed for the determination of sodium and potassium in physiological fluids and of lithium in serum and urine. Digital readout in mEq/liter.
Lower Detectable Limit	Li: 0.7 ppm Na: 2.0 ppm K: 4.0 ppm
Range	Sodium (1:200 dilution): 0-40.0 mEq/liter and 0-400 mEq/liter Potassium (1:200 dilution): 0-40.0 mEq/liter and 0-400 mEq/liter Lithium (1:10 dilution): 0-4.00 mEq/liter and 0-40.0 mEq/liter
Interferences	
Multiparameter Capability	
Sampling	Method: Batch Volume: Na & K minimum 0.2 ml after dilution; Li minimum 1.0 ml after dilution Capacity: 7+ samples/minute Aspiration Rate: 20-40 seconds/ml sample
Performance	Electronics: Solid state Linearity: 0.5% Stability: Scale Expansion: See "Range" Detector: Photomultiplier Zero Drift: Span Drift: Monochromator: Wavelength Range: Fixed: Interference filters K (766.4 nm), Li (670.8 nm), Na (588.9 and 589.5 nm) Bandwidth: Resolution: Dispersion: Slit Width: Gas Control: Oxidant: Air, built-in compressor Fuel: Instrument grade propane or dry natural gas Venting: Altitude: To 8,260 ft above sea level
Operation	Calibration: Standard solutions Procedure: Direct concentration readout after calibration Training: Manual included Unattended Period: Maintenance: Minimal, available through distributors and manufacturer

Requirements	Power: 105 to 130 Vac, 48 to 65 Hz, 300 W Weight: 34 kg (75 lb) Dimensions: Control console -- 37 cm W, 41 cm D, 24 cm H (14.5" W, 16" D, 9.5" H) Flame unit -- 29 cm W, 45 cm D, 47 cm H (11.5" W, 17.5" D, 18.5" H)
Features	Built-in compressor for air, electric flame ignition, safety circuits, flame state and out-of-range indicators Output: Rear panel analog voltage and BCD digital Options: Automatic dilutor for clinical flame photometry $452 Propane accessory 38
References	Manufacturer's Bulletin
Cost	Model 510 $3,950
Address	Turner Associates, Division of American Sterilizer Company 2424 Pulgas Avenue Palo Alto,CA 94303 (415) 324-0077

Ultraviolet/Visible Spectrophotometer
Varian, Cary 17





Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Double monochromator, double beam, coupled scan and chart drive, measures absorbance and transmittance, adapts for reflectance, fluorescence or derivative spectra.
Lower Detectable Limit	
Range	Absorbance: 0-1, 1-2, 0-0.5, 0.5-1, 0-0.2, 0.2-0.4, 0-0.1 and 0.1-0.2 Transmittance: 0-100%, optional 5, 10, 20, 50% T
Interferences	
Multiparameter Capability	Auto sample changer, digital repetitive scanning, fluorescence, scattered transmission, reflectance, derivative spectra.
Sampling	Method: Batch Volume: As small as 20 µl Capacity:
Performance	Electronics: Solid state Linearity: 0.0005 A at 0.1 absorbance Stability: Scale Expansion: Detector: Photomultiplier Zero Drift: <0.0005 absorbance/hr drift with standard VIS-IR source 0.001 with standard UV source Span Drift:
	Monochromator: Prism and grating Grating: 600 lines/mm Prism: 30 degree fused silica Wavelength Range: 186-2650 nm Wavelength Accuracy: at least ±0.4 nm Wavelength Reproducibility: at least 0.05 nm in UV-VIS, 0.25 nm in near IR Resolution: 0.1 nm in "most of" UV-VIS, 0.3 nm in near IR Dispersion: Slit Width: 0 to 3 mm, servomotor control Stray Light: <0.001% from 210 to 1800 nm Temperature Coefficient: 0.03 nm/°C
Operation	Calibration: Standard samples Procedure: Manual provided Training: Requires about hours Unattended Period: Maintenance: 27 service centers in U.S.
Requirements	Power: 115 or 230 volts, 50 or 60 Hz, 11 amps Weight: 317 kg (700 lbs) Dimensions: 144 cm W, 93 cm H, 84 cm D (57" W, 36.5" H, 33" D)
Features	Output: Built in recorder

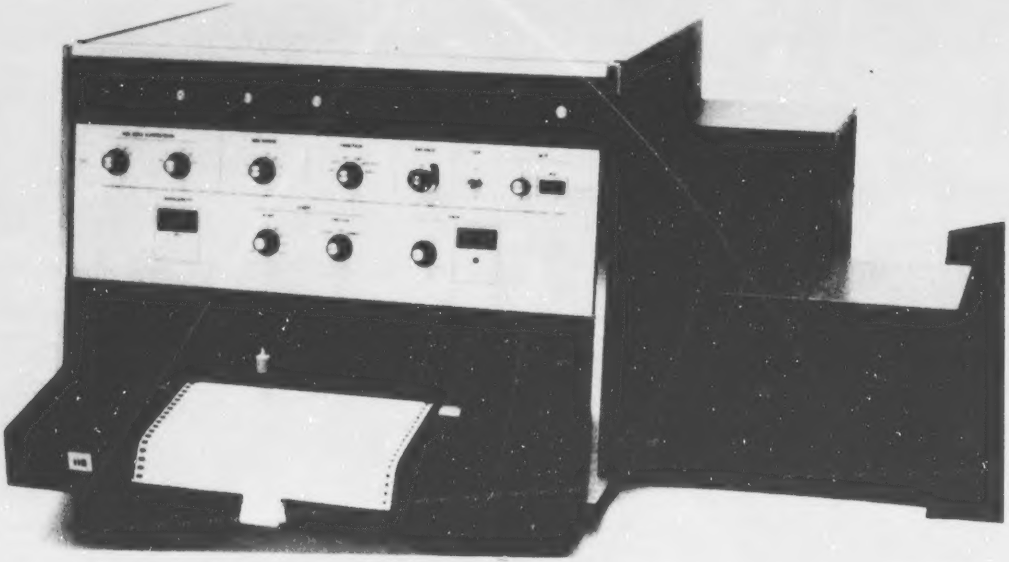
Options:	Automatic Sample Changer, Model 1729000	$3,045
	Digital Repetitive Scan Accessory, Model 1718000	2,095
	Fluorescence Accessory, Model 1712000	3,335
	Fluorescence Excitation Accessory, Model 1412800	970
	Diffuse Reflectance Accessory, Model 1711000	5,775
	Specular Reflectance Accessory, Model 1413000	4,085
	Cell Space Diffuse Reflectance Accessory, Model 1411750	1,280
	Scattered Transmission Accessory, Model 1762000	3,875
	Derivative Accessory, Model 1790900	875

References	a) Manufacturer's bulletin b) Price list, July 1975	
Cost	Model 17	$29,990

Address

Varian, Instrument Division
611 Hansen Way
Palo Alto, CA 94303
(415) 493-8100
Box D-070

Ultraviolet/Visible Spectrophotometer
Varian, Cary Model 118A, 118B, 118C



Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Double monochromator. Measures directly the ratio of the sample beam intensity to the reference beam. Single detector. Five digit photometer readout. Deuterium and tungsten halogen lamp sources. Computer compatible so that closed loop operation is possible. 118A -- manual 118B -- ratio recording 118C -- ratio recording/scanning
Lower Detectable Limit	
Range	Absorbance: 0 to 0.02, 0.05, 0.10, 0.20, 0.50, 1.0, 2.0, 3.0 % Transmission: 0-10%, 0-100% Concentration: Adjustable to read 0-12,000 units
Interferences	
Multiparameter Capability	Fluorescence, scattered transmission, difference spectra
Sampling	Method: Batch Volume: As small as 20 µl

Performance

Electronics: Solid state

Linearity: ±0.0004 A
Stability:
Photometric Accuracy: 0.001 A @ 1 A, 0.004 A at 0.1 A
Scale Expansion: 30 x in concentration mode
Detector: Photomultiplier

Zero Drift: < 0.0004 A/hour
Span Drift:

Monochromator: Dual prism

Prism: Dual 30° fused silica
Wavelength Range: 185-800 nm; 170-600 nm with low UV detector
Wavelength Accuracy:
Resolution: 0.03 nm at 200 nm; 0.1 nm @ 350 nm
Dispersion:
Stray Light: < 0.001% over most of range; < 0.1% at 170 nm, 800 nm
Slit Width: 0-3 nm

Operation

Calibration: Standard solutions
Procedure: Manual provided
Training: Requires about hours
Unattended Period:
Maintenance: 27 service centers in U.S.

Requirements

Power: 115 or 230 ± 10% Vac; 50 or 60 ± 1% Hz; 5A maximum
Weight: 227 kg (500 lb) shipping weight
Dimensions: 118A -- 115 W x 50 H x 57 cm D (46 x 20 x 23 in.)
118B and 118C -- 115 W x 50 H x 80 cm D (46 x 20 x 28 in.)

Features

Output: Built-in recorder, high intensity lamp

Options:	
Automatic Sample Changer, Model 1829000	$3,190
Digital Repetitive Scan, Model 1818000	1,695
Dual Wavelength Drive, Model 1841700	1,390
Fluorescence Excitation Model 1812800	695
Multi-Zero Suppression, Model 1827000	1,740
Scattered Transmission, Model 1862000	4,055

References

a) Manufacturer's Bulletin
b) Price List, July 1975

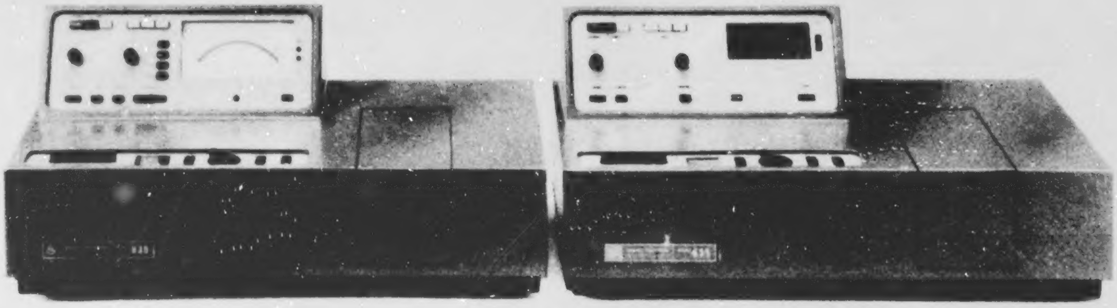
Cost

Model 118A	$11,900
Model 118B	$15,525
Model 118C	$17,250
Model 118C with special UV Detector (170-600 nm)	17,785

Address

Varian
Instrument Division
611 Hansen Way
Palo Alto, CA 94303
(415) 493-8100

Ultraviolet/Visible Spectrophotometer
Varian Techtron, 635 Series



Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Double beam; meter readout. Model 635D has digital readout. Light from lamp source is passed alternately through the sample and reference 30 times per second, and the ratio of the two intensities is read out. Single beam operation is available. Automatic or manual wavelength scanning.
Lower Detectable Limit	
Range	Absorbance: 0-0.1, 0-0.5, 0-1.0, 0-2.0 % Transmission: 0-100% Concentration: Any range
Interferences	
Multiparameter Capability	Fluorescence - total and spectral; multiple sample handling; kinetics accessories; gel scanning
Sampling	Method: Batch and automatic, Auto 50 sampling system Volume: 1 ml to 50 ml Capacity: 3 samples/minute

Performance

Electronics: Solid state modules
Linearity:
Stability:
Scale Expansion: Any 0.1 segment of absorbance range between 0 and 1.5 can be expanded to full scale.
Detector: Photomultiplier

Zero Drift: <0.002 A/hour
Span Drift: <0.0004 A/hour

Monochromator: Czerny-Turner mounting
Grating: 32 x 27 mm; 12,767 grooves/mm; blazed at 275 nm
Wavelength Range: 190-900 nm
Wavelength Accuracy: >±0.5 nm
Resolution: 0.2 nm
Bandpass Width: 0.06 nm
Dispersion: 3.3 nm/mm
Stray Light: <0.1% at 220 nm
Slit Width: Step adjustable 0.2, 0.5, 1.0 and 2.0 mm

Operation

Calibration: Manual -- one control
Procedure: External standards; wavelength by internal standards
Training: One hour required
Unattended Period: Two hours
Maintenance: 27 service centers in U.S.
Temperature Compensation: Both wavelength and electronics

Requirements

Power: 110, 115, 220 or 240 Vac; 50 or 60 Hz; 200 W maximum
Weight: 34 kg (75 lb)
Dimensions: 72 cm W x 40 cm D x 33 cm H
(28-1/2" x 15-3/4" x 13")

Features

Output: Analog Meter; 0-10 mv. Recorder; Digital Display

Options:	Automatic Sampler, Model Auto-50	$2,080
	Digital Printer, Model 36	2,615
	Automatic Wavelength Programmer	1,755
	Fluorescence, total	235
	Reflectance, diffuse	1,705
	Recorder, Model 135-1	1,010
	Auto-5 Cell Programmer	2,235
	Gel Scanner	1,460
	Data Acquisition, Model 35	3,940

References

a) Manufacturer's bulletin

b) Price List, Sept. 1975

Cost

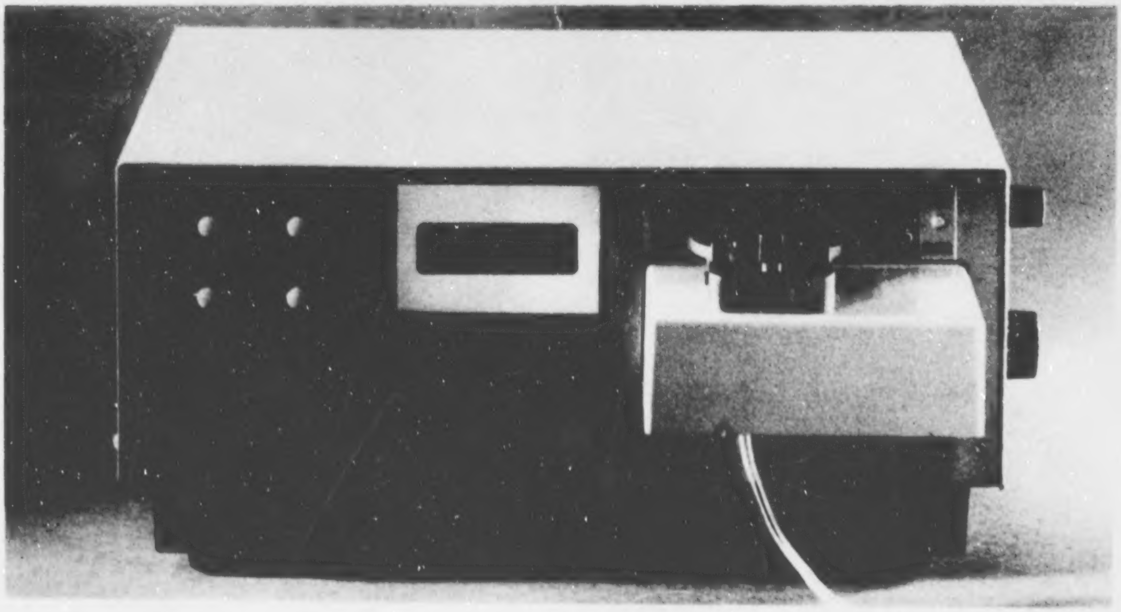
Model 635M	$5,300
Model 635D	6,400

Address

Varian Techtron
611 Hansen Way
Palo Alto, CA 94303
(415) 493-8100

Ultraviolet/Visible Spectrophotometer

Zeiss, Model PM2 D



Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Single beam. Digital readout. Grating monochromator.
Lower Detectable Limit	
Range	Absorption: Concentration: Transmission:
Interferences	
Multiparameter Capability	
Sampling	Methods: Batch, solutions Volume: 0.5 ml min. Capacity: Approx. 30 samples/minute or flow-through operation Temperature Compensation: Control available

Performance

Electronics:

Linearity: Better than 0.3% of full scale
Stability: Better than 1.0%/hour
Scale Expansion: 10x
Detector: Photocell 200-850 nm
Zero Drift: 0.1%/hour
Span Drift: 0.5%/hour

Monochromator:

Grating: 600 lines/mm
Wavelength Range: 200-1000 nm
Bandwidth: 10 nm
Resolution: 10 nm
Wavelength Accuracy: 1 nm
Slit Width: Fixed
Stray Light: Less than 0.5% from 200-850 nm

Operation

Calibration: Standard samples
Procedure: Semi-automatic
Training:
Unattended Period:
Maintenance:

Requirements

Power: 110 V; 60 Hz, 60 VA
Weight: 16 kg (35 lbs)
Dimensions: 47 x 47 x 22 cm (18.5 x 18.5 x 8.7 in.)

Features

Output: 0-1 analog, BCD
4-digit indicator for A, C, %T
Automatic blank adjustment available

References

a) Manufacturer's bulletin "PM2 Spectrophotometer"
b) Price list, January 1974

Cost

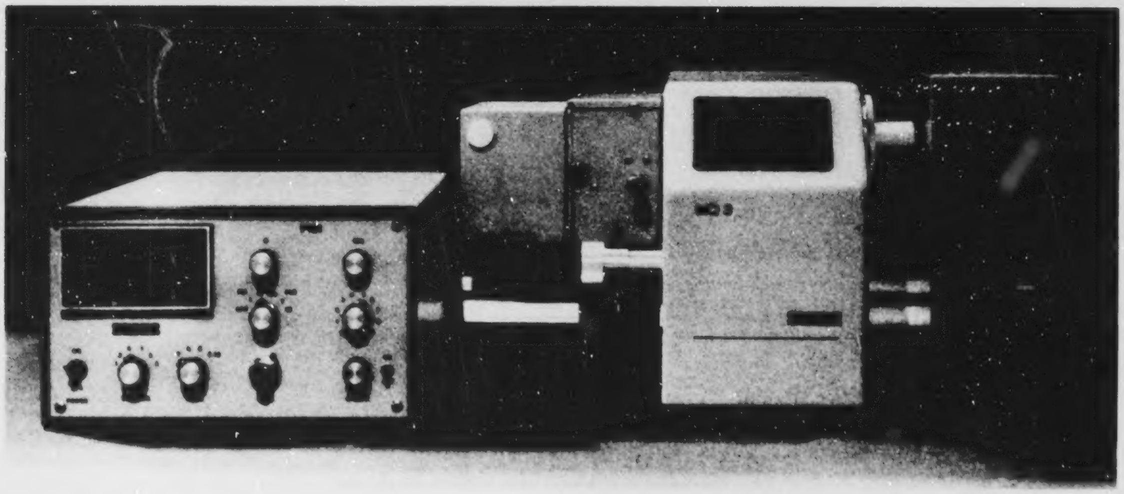
Model PM2 D $2,485

Address

Carl Zeiss, Inc.
444 Fifth Avenue
New York, NY 10018
(212) 730-4400

H2O-MET
UV-Visible
Carl Zeiss 2
Sept. 1975

Ultraviolet/Visible Spectrophotometer
Zeiss, Model PMQ 3



Class	Laboratory
Categories	Air: Source, Vehicular, Ambient Water: Fresh, Saline, Waste Biomedical: Blood, Tissue, Serum, Urine
Principle of Operation	Single beam. Digital meter readout. Prism monochromator.
Lower Detectable Limit	Nanogram range (depending on compound)
Range	ppb to %: 1 ppb - 100% (depending on compound)
Interferences	
Multiparameter Capability	Reflectance, flame, fluorescence, TLC, gel, absorbance, transmission, concentration
Sampling	Method: Batch, solutions and solids Volume: 0.06 ml Capacity: 60 samples/minute with automatic changer; flow-cell equipment available
Performance	Electronics: Linearity: 0.1% Stability: ±0.1%/hour Scale Expansion: 0-10x Detector: Photomultiplier R 446 (185-850 nm) PbS cell (620-2500 nm) Zero Drift: ±0.1%/hour Span Drift: ±0.1%/hour Monochromator: Prism: M4QIII 30° quartz, Littrow mounting Wavelength Range: 185-2500 nm Resolution: 0.03 nm in U.V., 1 nm @ 600 nm Accuracy of Wavelength Setting: <0.05 nm @ 200 nm Dispersion: @ 200 nm = 1.5 nm/mm Slit Width: Continuous between 0-2 nm Stray Light: <0.1% between 200 and 1000 nm

Operation	Calibration: Internal calibration standards and automatic blank control Procedure: Training: Unattended Period: Maintenance: Temperature Compensation: Temperature control available
Requirements	Power: 110 V; 60 Hz; 370 VA Weight: 54.5 kg (120 lb) Dimensions: 70 x 50 x 25 cm (27.5 in., 19.7 in., 9.8 in.)
Features	Output: Analog 0 - 1 V. Linear for %T, A, C. Digital BCD. Display: 4 digits.
References	a) Manufacturer's bulletin "Zeiss PMQ 3 Spectrophotometer" b) Price list, January 1974
Cost	Model PMQ 3 $7,984
Address	Carl Zeiss, Inc. 444 Fifth Avenue New York, NY 10018 (212) 730-4400

C.3. CONTENTS FOR

X-RAY FLUORESCENCE ANALYSIS

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III. General Measurement Considerations

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- B. The Detector and Analyzer
- C. Excitation of Fluorescence Radiation

IV. Excitation Sources

- A. Radioactive Sources
- B. X-ray Tube Excitation
- C. Filters for Tuning the Excitation Energy
- D. Charged Particle Excitation

V. Energy Selective Systems

- A. Silicon Semiconductor Detectors
- B. Other Energy-Dispersive Detectors
- C. Si(Li)-Detector System Performance
- D. Wavelength Dispersive Systems

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VII. Acknowledgment

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IX. Commercially Available Instrumentation

X-RAY FLUORESCENCE ANALYSIS

I. INTRODUCTION

X-ray fluorescence analysis resembles visible-light or ultraviolet emission spectroscopy in its basic principles. In both of these analytical methods, electrons in the material to be analyzed are excited into higher energy states by radiation. Upon return to their ground states (or lower energy levels) characteristic electromagnetic radiation is emitted which when analyzed serves to identify the materials involved.

X-ray fluorescence analysis differs from emission spectroscopy in two profound respects. First, the radiation involved is of very much higher energy (shorter wavelength) so that entirely different means of excitation, analysis, and detection of the radiation are used. Second, the electronic transitions involved generally lie deep within the atom, so that they are little affected by the chemical state of the atom. Thus the method serves to identify the atoms of which the sample is constituted, but is insensitive to the chemical state of the atom.

The analysis of the atomic (elemental) composition of materials by x-ray fluorescence has a long and distinguished history. For many years, the technique has been widely applied in commercial fields such as metallurgy, mineral assay, and chemical process control. For measurements of trace concentrations in environmental samples, however, it has only recently become prominent. This prominence, increasingly important as environmental trace measurement needs have expanded, is mainly due to a number of recent technical developments which now allow rapid, multi-element determinations in the parts-per-million (ppm) range.

In this section of the Survey we shall discuss in some detail the application of x-ray fluorescence to the determination of concentrations of trace elements in environmental samples. Although the technique is applicable to a wide variety of solids, here we shall consider mainly air particulate samples and dried biological materials.

Sample collection and preparation will not be discussed in detail here. It should be borne in mind that for many types of samples, the errors due to possible difficulties and uncertainties in collection and preparation can be much more important than the analytical errors. The sampling of aerosols has been discussed elsewhere in this Survey. The emphasis of this narrative will be on the advantages and limitations of various x-ray fluorescence methods.

The reader is referred to a number of review articles and books for details on the basic methods of this type of analysis. The review articles by Goulding and Jaklevic (Ref. 1), Giauque et al. (Ref. 2), and Rhodes (Ref. 3, 4) and the books by Woldseth (Ref. 5) and Russ (Ref. 6) are particularly useful for energy-dispersive analysis. For wavelength-dispersive analysis the books by Liebhafsky et al. (Ref. 7), Bertin (Ref. 8), and Jenkins and DeVries (Ref. 9) are recommended.

II. PRINCIPLES OF X-RAY FLUORESCENCE

The basic principle of x-ray fluorescence is simple and is illustrated in Fig. 1 (Ref. 2). (This illustration shows a typical energy dispersive system, but the principles are similar for wavelength-dispersive systems.) Exciting radiation impinges on a specimen. If the radiation is sufficiently energetic, some of the interactions will result in the excitation of electrons out of the inner shells of the atoms within the specimen. As an individual atom returns to the ground state (or to any lower-energy state), it may undergo any of several types of transformations. One of these is the emission of a fluorescent x-ray as an outer orbital electron fills the vacancy; the x-ray possesses a wavelength (and energy) characteristic of the particular transition, which in turn is characteristic of the particular atom involved. The x-rays are detected and their wavelength or energy measured, the intensity being nominally proportional to the atomic concentration in the specimen.

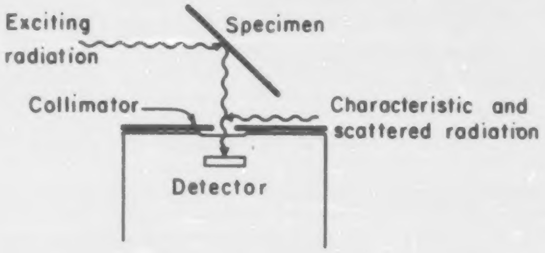


Figure 1. Schematic of x-ray fluorescence analysis technique showing typical energy-dispersive set-up (from Ref. 2).

The sensitivity and specificity of the technique are dependent upon a number of factors. The two fundamental physical factors are the probability that the incident radiation will produce the desired vacancy, and the probability that the resulting readjustment of the atom will produce fluorescent x-ray emission. The main instrumental factors are that the incident radiation intensity be sufficient to provide enough fluorescence to be measurable above whatever background may be present; and that the wavelength or energy resolution of the spectrometer be sufficient to resolve closely spaced x-ray lines in order to identify the elements in the specimen.

Four basic design parameters in the system are: choice of exciting radiation (type, intensity, energy distribution); choice of means for spectrum analysis; choice of detector (type, operating parameters); and choice of geometrical layout. Each of these choices may be made so as to optimize one or more of the above parameters, frequently at the sacrifice of some others. A number of other factors must be considered in the choice of instrumental method: foremost among these are the accuracy and precision of the determinations, the cost and time required, possible multi-element capability, ease of calibration, and destruction or non-destruction of the specimen.

The choice of exciting radiation influences every other parameter. The most common x-ray fluorescence systems use photons as the exciting radiation, either x-radiation directly from x-ray tubes, secondary fluorescence x-rays produced by employing secondary targets to modify the direct x-ray tube output, or gamma-rays or x-rays from the decay of a radioactive source. Other types of exciting radiation include accelerator-produced protons and alpha particles.

There are two different types of x-ray analyzers in common use: crystal diffraction spectrometers which rely on Bragg diffraction to separate lines by wavelength dispersion, and semiconductor spectrometers which absorb the x-ray, producing a pulse of electronic charge proportional to the x-ray energy. These two systems rely upon different physical principles for their operation, and have very different properties.

We shall discuss the wavelength dispersive and energy-dispersive systems separately, in each case emphasizing photon-induced excitation. Excitation by particles will be discussed as it is applied to energy-dispersive detectors.

III. GENERAL MEASUREMENT CONSIDERATIONS

Here we will discuss various considerations which are common to all of the x-ray fluorescence methods, concerning sample preparation, detectors and analyzers, and excitation radiation.

A. The Sample

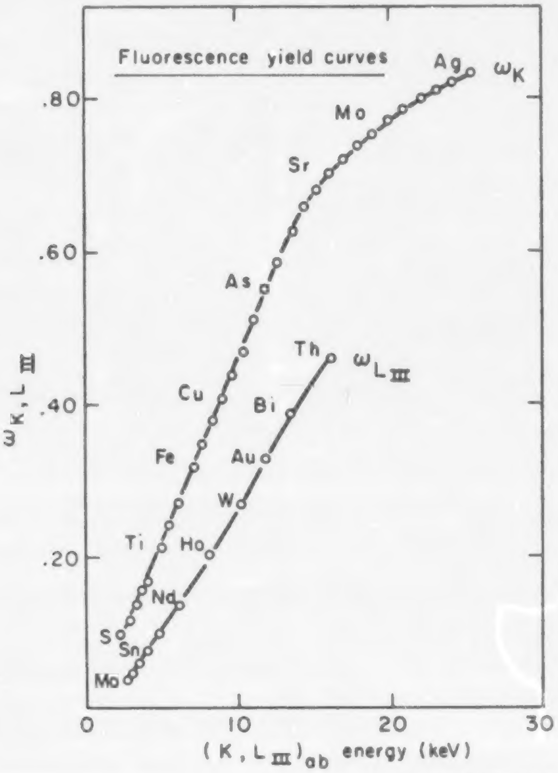
A few general considerations which apply to all x-ray fluorescence systems will be discussed here. The first area concerns the sample being examined. There are two important parameters involved here: the type of atom being sought and the quantity of material involved.

The primary consideration in any measurement is the magnitude of the parameter(s) being measured. Here we are mainly considering measurements of the trace elemental concentrations in air particulate samples and dry (or dried) biological samples. The concentrations are usually expressed as parts-per-million (ppm) in samples other than air particulate samples collected on filters; for the latter the desired quantity is weight per unit volume of sampled air (for example, nanograms/cubic meter, ng/m^3).

A typical air filtering system might sample enough air to pass about one cubic meter of air through each cm^2 of air filter surface area. (For example, a sampling rate of 1 liter/second for 2 hours yields 7.2 m^3 of air; a typical air filter might have 8 cm^2 of area, producing 0.9 m^3/cm^2.) This typical value, $\sim 1\ m^3/cm^2$, may vary as much as a factor of 5 either way, but seldom more in actual sampling set-ups. For a value of 1 m^3/cm^2, an x-ray fluorescence measurement of, say, 1 ng/cm^2 on the air filter corresponds directly to 1 ng/m^3 in the sampled air, which provides an easily remembered conversion.

For biological samples, the sample thickness is usually the important parameter. Suppose a sample is prepared with a thickness of 10 micrometers (10 μm), which equals 10^{-3}cm. Then 1 cm^2 of area has beneath it 10^{-3} cm^3 of volume. Hence, 1 ng/cm^2 (10^{-9} g/cm^2) corresponds to 10^{-6} g/cm^3. If the basic substrate has unit density of one $gram/cm^3$ (typical of biological speciments) then 1 ng/cm^2 corresponds to 10^{-6} g/g, or 1 ppm. The conversion is again easy to remember: for 10 μm thickness, 1 ng/cm^2 measured corresponds to 1 ppm.

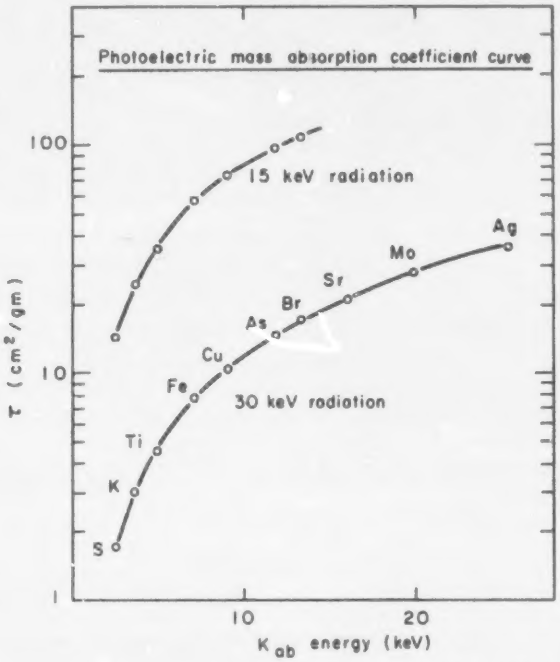
Both the fraction of the time that the return of excited electrons to their ground state produces fluorescent radiation, and the wavelength (energy) of this radiation are determined by the atomic number of the element involved. When the excitation produces a vacancy in one of the inner electron shells, there are two dominant processes whereby the atom returns to its ground state. These are the emission of fluorescent x-rays (desired in this application) and the emission of Auger electrons (undesired in this application). The fraction of excitation producing fluorescent radiation is termed the "fluorescent yield", which is shown for the K and L_{III} lines in Figure 2 (Ref. 2). It should be noted that the fluorescent yield is low for the very low atomic number atoms. It should also be noted that the energy of the fluorescent x-rays from these light atoms is low. Both of these factors increase the difficulty of performing x-ray fluorescence analysis of elements with low atomic numbers.



XBL725-2949

Figure 2. Theoretical fluorescence yield curves for the K and L_{III} energy levels (from Ref. 2).

A second, and equally important, physical parameter relates to the excitation of atoms in the sample. When (as is usually the case) x-rays or gamma rays are the excitation source, the important parameter is the photoelectric cross-section, usually parameterized by the photoelectric mass absorption coefficient. For any given photon energy, the absorption coefficient is greatest for the element whose K (or L) absorption edge is just below the given photon energy. (If the edge exceeds the given energy, the photoelectric effect is energetically impossible for that electron shell.) Figure 3 (Ref. 2) shows examples of photoelectric cross-section curves for 15 keV and 30 keV radiation. Note that, for example, bromine (Z = 35) has a much higher cross-section at 15 keV than at 30 keV, since its K absorption edge is at 13.45 keV. The difference is about a factor of 6.



XBL725-2950

Figure 3. Photoelectric cross-section curves for 15 and 30 keV photons (from Ref. 2).

A third general consideration has to do with specimen thickness. Because some of the energies involved are low, both the incident and fluorescent photons can have relatively high mass absorption coefficients in matter. This means that if a sample is too thick, the part of it that is well below the surface will not be reached by much of the exciting radiation, nor will many of the fluorescent x-rays emerge. For such thick samples, the analysis is only sensitive to a complicated integral of the composition at and near the surface. In the usual geometrical set-up, in which fluorescent radiation is detected as it leaves the sample on the same side which is irradiated, one way of expressing this is by a criterion such as the following: Let m be the mass per unit area of the specimen, and μ be the sum of the incident and fluorescent mass absorption coefficients (μ_I and μ_F). Then in a simplified way, the fraction of photons surviving unabsorbed is $e^{-\mu_I m}$ (incident) and $e^{-\mu_F m}$ (fluorescent), the product being

$$e^{-(\mu_I + \mu_F)m} = e^{-\mu m}$$

One criterion might be to consider a sample "thin" if the product (μm) is less than, say, 0.1, in which case the fraction absorbed would be $(1 - e^{-0.1})$ or about 9.5%. This is shown in Figure 4 (Ref. 4) for excitation with energies of 42, 22, 15 and 5.9 keV.

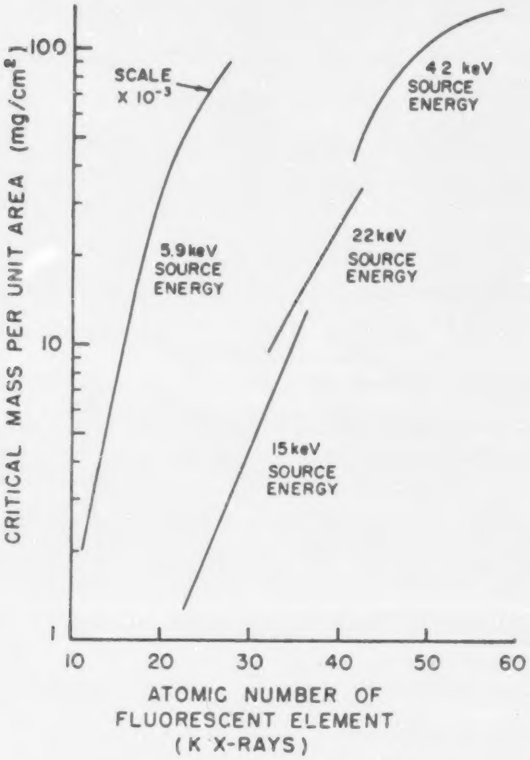


Figure 4. "Critical thickness" as a function of atomic number. This is the thickness at which the fraction of x-rays absorbed is about 10% (from Ref. 4).

A factor can, of course, be applied to the analytical data to correct for this absorption effect if the specimen thickness is well known. This factor would take into account the geometrical layout as well as the energy dependences, and has been discussed by Giauque et al. (Ref. 2).

Usually, air filters taken as environmental samples are thin enough to meet the above thickness criterion. (For low-Z elements, however, even air filters do not meet the criterion.) However, other samples (for example, biological samples) must be prepared as thin specimens for x-ray fluorescence analysis, unless analysis only for an integral of the composition in the surface region explored by the x-rays is sufficient.

For particulate specimens containing high-Z elements (including some dried solution samples as well as aerosol particulate samples), absorption in individual particles may be a problem if the particles are sufficiently large, even though the total specimen thickness can be well below the criterion value just discussed. If μ' is the linear absorption coefficient (cm^{-1}), then transmission from the center of a particle of radius r is roughly $e^{-\mu' r}$. Hence, if $\mu' r$ is small enough (smaller than, say, 0.1) the absorption will not be large and the analysis will be nearly uniformly sensitive for the entire particle in question.

Another key consideration in obtaining high analytical sensitivity with very thin specimens is the composition and thickness of the specimen substrate. Obviously, it should be as free as possible of the trace elements being analyzed. Generally, it is desirable that the substrate be as thin as possible and be composed of low-atomic-number elements. For air filters, this criterion is best met with a clean organic substrate. Examples are cellulose, polycarbonate, teflon, and polypropylene. A comparison between a typical cellulose filter and a typical glass fiber filter is shown in Figure 5 (Ref. 10). These data were taken using excitation radiation from a cadmium-109 source (22 and 25 keV photons), and with an energy-dispensive silicon detector spectrometer. Note the significant contamination of several elements in the glass fiber filter.

B. The Detector and Analyzer

The detection of x-rays and gamma rays has been discussed in some detail in the volume of this Survey on RADIATION. Detection techniques can be divided into four classes: photographic, gas ionization, scintillation,

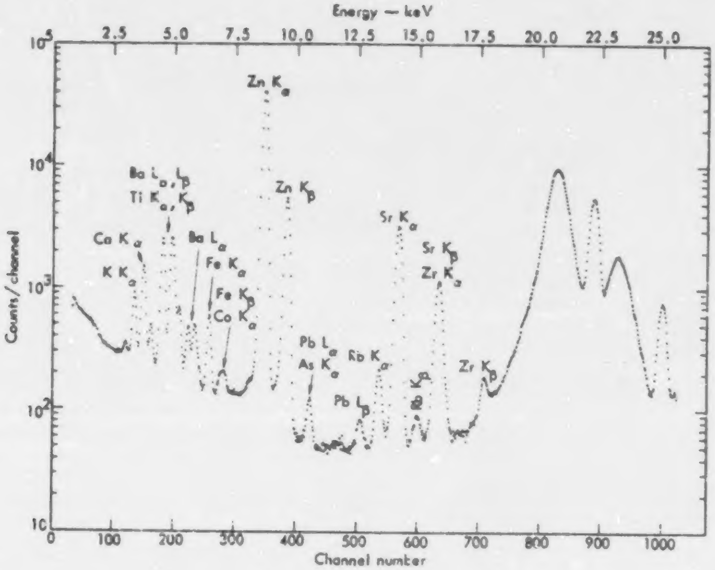


Figure 5(a). Background spectrum of a typical glass fiber filter, 10 ksec count, ^{109}Cd. Note the large number of interfering peaks (from Ref. 10).

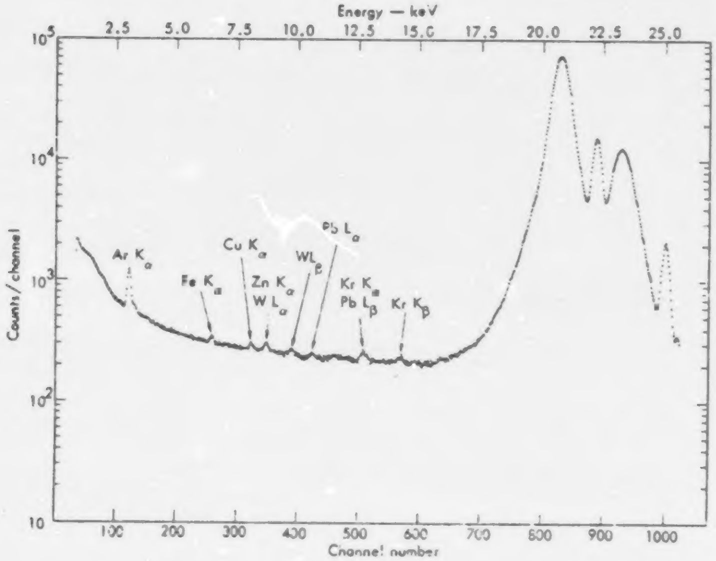


Figure 5(b). Background spectrum of Whatman 41 paper, 50 ksec count, ^{109}Cd (from Ref. 10).

and semiconductor detection. The gas ionization detectors can further be divided into ionization chambers, proportional counters, and Geiger-Mueller counters.

The spectral analysis by photon energy can be achieved by using x-ray crystal diffraction with one of the detectors listed above or by using the energy resolution capabilities of semiconductor detectors. (Note: This property is shared by the scintillation counters and the gas proportional counters, but the energy resolution of these two devices is not sufficient for them to be useful as spectrum analyzers in this application.)

The resolution with which various detector systems can measure a particular monoenergetic line is a very important consideration. A comparison has been made by Rhodes (Ref. 3) and is shown in Figure 6, which also shows the separation of K_α lines for adjacent elements $\Delta K_\alpha(Z)$ plotted against $K_\alpha(Z)$ energy, as an indication of the resolving power requirements. Note that the good resolution of the crystal diffraction technique at low energies far exceeds that of any other detectors. The lithium-drifted silicon detectors, denoted Si(Li), are shown with the resolutions achieved as of 1969. Since that time, better resolutions (by a factor of perhaps 2) have been obtained. While the gas proportional counters are incapable of separating adjacent lines, lacking sufficient resolution by about a factor of 2 to 3 over the entire energy range, they are still useful when studies do not require such separation.

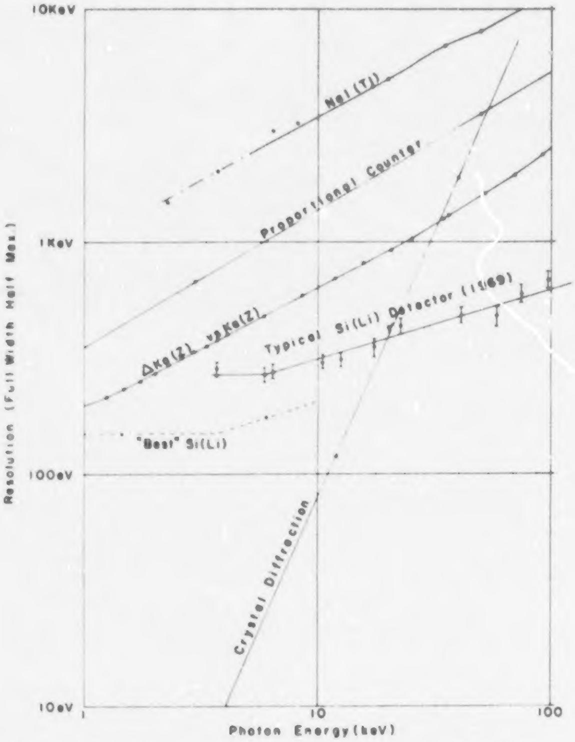


Figure 6. Energy resolution of various detectors compared with separation between K x-rays from adjacent elements. These data were compiled in 1969. Since then the "best Si(Li)" detectors have improved about a factor of 2 in resolution (from Ref. 3).

Energy dispersive x-ray fluorescent systems have only recently come into common use for trace element analysis. The development of the semiconductor detector is responsible for this. Today, energy-dispersive x-ray fluorescence analysis is most commonly performed with silicon semiconductors.

One of the advantages as well as disadvantages of the energy-dispersive systems is that the detector is directly exposed to every type of radiation emerging from the irradiated specimen. (This is not true of wavelength-dispersive systems, in which only a narrow part of the entire spectrum normally strikes the detector.) Many of the features which characterize the modern semiconductor systems have been developed in order to overcome the undesirable side-effects of this full exposure.

Suppose that the exciting radiation is ideal monochromatic x-radiation. Its interaction in the specimen produces a spectrum of pulse-heights (energies) at the output of the semiconductor detector which is shown in stylized fashion in Figure 7 (Ref. 2). The highest-energy photons are those scattered from the specimen coherently without energy loss (Rayleigh scattering). Just lower in the pulse-height distribution is a larger peak due to incoherent (Compton) scattering, in which there is some energy loss as the photon scatters from an atomic electron. When there are only trace concentrations in a low-Z matrix, these two types of events are usually more probable by far than the fluorescence x-rays which appear as the lower-energy peaks. Notice that there is a small continuum of events below the incoherent peak, due partially to incomplete charge collection in the semiconductor for events which would otherwise be in the high-energy peaks. For the system to be useful, the fluorescent x-rays must stand out above this background. Lower still is a large number of events in a spectrum

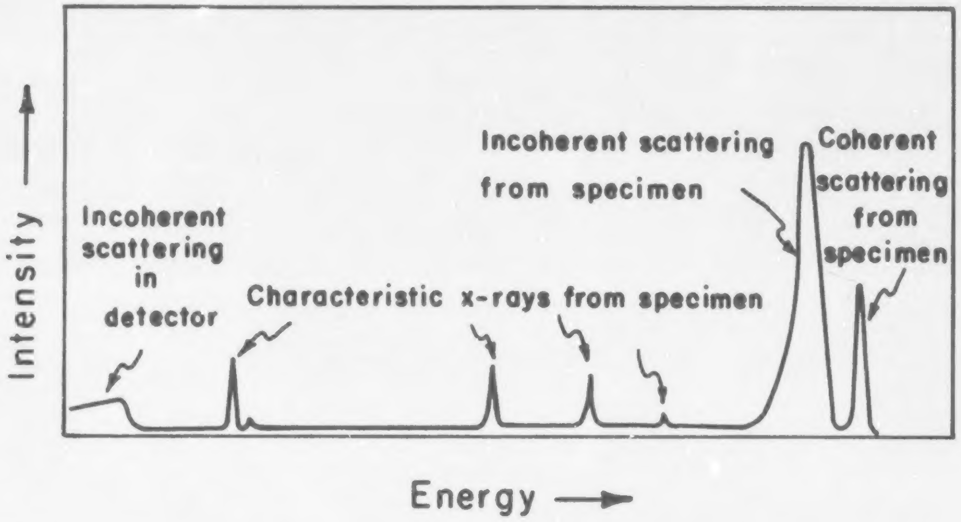


Figure 7. Generalized energy spectrum obtained from a low atomic number matrix with a semiconductor detector. The exciting radiation is assumed to be monochromatic (from Ref. 2).

which has a relatively flat distribution with a maximum energy cut-off. These are due to Compton scattering in the detector of some of the photons which would have appeared in the coherent or incoherent peaks if they had been totally absorbed by photoeffect. This Compton scattering results in the deposition in the detector of only a fraction of the photon energy. The remaining energy escapes as a lower energy photon.

C. Excitation of Fluorescence Radiation

The most desirable radiation for exciting fluorescence from a given element would consist of monoenergetic photons with energy slightly above the most energetic transition being sought. Practical systems cannot provide perfectly monochromatic x-radiation for excitation of the specimens. The closest approach is the use of a radioactive source which decays by emitting either a single or a group of closely spaced gamma-ray or x-ray lines. The common bremsstrahlung x-ray tube may also be used as an excitation source, but the x-radiation consists of a continuum of energies roughly in a 1/E spectrum, where E is the energy of the primary electron beam in the tube. The very high x-ray intensities available with such a tube are balanced by a loss of sensitivity because of the continuous distribution of the exciting radiation, which increases the background and decreases the fluorescent signals. A more nearly "monoenergetic" technique is use of a secondary-fluorescent target: primary electrons or radiation from a primary x-ray tube excite x-ray fluorescence in the target, and these secondary x-rays are then used as the exciting radiation for the analytical measurements. Another method for generating nearly monochromatic photons is use of a crystal-diffraction monochromator in conjunction with an x-ray tube. By selecting the appropriate geometrical layout, only a narrow energy band is Bragg-diffracted toward the specimen to be analyzed.

Other techniques which have been introduced for improving the energy distribution from the x-ray tube beam include transmission target x-ray tubes and the use of filters. Because each of these modes of excitation has an important effect on the other parameters of the system, we will discuss each separately in the next section.

IV. EXCITATION SOURCES

A. Radioactive Sources

Use of a radioactive material as the source of exciting radiation has the advantage that such a source produces a predictable, constant, calibrated intensity with a known energy spectrum. These sources tend to be inexpensive to purchase and maintain, with the obvious disadvantages that they are considerably less intense than x-ray tubes, that they cannot be 'turned off' when not in use, and that their intensity cannot be easily varied. (In actual fact, sources in common use do not pose a serious radiation hazard even when unshielded, unless extremely lax safety procedures are employed.)

The most useful radioactive sources are, for most applications those which produce monoenergetic photons, either as gamma rays from nuclear decay or as x-rays following electron caputre. Because (as discussed above) the maximum sensitivity occurs when the exciting radiation's energy is just above the absorption edges of the elements of interest, it is usually necessary to use more than one source in order to cover a wide range of elements efficiently. Another approach is use of a bremsstrahlung source (in which beta particles radiate photons as they decelerate) to achieve a continuous distribution of excitation energies, but this method usually involves a sacrifice in sensitivity.

Table 1 (from Ref. 3) lists some of the radioactive sources which have been found useful. The source activities shown each produce about 10^8 high-energy photons per second. Generally, analysis in the parts-per-million region requires sources of at least this size (the fractional-curie range) in order to perform the analyses in times of a few minutes, coupled with a high-efficiency source-specimen-detector geometrical layout.

TABLE 1.

Relevant Properties of Primary X-ray and Gamma Ray Sources (from Ref. 3).

Isotope	Half-Life, Years	Mode of Decay	Photon Emission			Normal Activity, mCi
			Energy (keV) and Type	Production,[a] %	Emission,[b] %	
^{55}Fe	2.7	electron capture	5.9, MnK X-rays	28.5	10 to 15	20
^{238}Pu	86.4	alpha	12 to 17, UL X-rays	10	5 to 10	30
^{75}Se	0.33	electron capture	10.5, AsK X-rays	40		
			140, gamma rays	54		
			270, gamma rays	56		
^{210}Pb	22	beta	11 to 13, BiL X-rays	24	10 to 15	10
			47, gamma rays	4		
			10 to 1000, bremsstrahlung	∿ 2		
^{109}Cd	1.3	electron capture	22.2, AgK X-rays	107	80	1
			88.2, gamma rays	4		
^{125}I	0.16	electron capture	27, TeK X-rays	138	100	1 to 10
			35, gamma rays	7		
^{241}Am	458	alpha	59.6, gamma rays	36	30	1 to 20
			14 to 21, NpL X-rays	37	0 to 20	
^{153}Gd	0.65	electron capture	103, gamma rays	20	∿ 20	1
			97, gamma rays	30	∿ 30	
			70, gamma rays	2.6	∿ 2	
			41, EuK X-rays	110	∿ 50	
^{57}Co	0.74	electron capture	136, gamma rays	8.8		1
			122, gamma rays	88.9	∿ 80	
			14, gamma rays	8.2		
			6.4, FeK X-rays	51	0 to 10	
^{137}Cs	30	beta	662, gamma rays	82	∿ 80	

[a] Theoretical yield, percent photons per disintegration.

[b] Approximate practical output, percent photons per disintegration.

[c] Also the use of ^{125m}Te, with similar characteristics to ^{125}I, has been reported.

When a semi-conductor detector is used, several source/specimen/detector geometrical arrangements are possible. Four of these have been discussed thoroughly by Rhodes (Ref. 3), and are shown in Figure 8. The "central source" geometry is most useful with large detector areas and small sources, and finds little application with the usual small-area semiconductor detectors. The "side source" geometry is useful when source and detector sizes are comparable. In either central or side arrangements, there is an optimum distance for maximum counting rate, which is different for different source energies. The "annular" configurations have been commonly used with the small semiconductor detectors. The source is either deposited as an annular ring, or assembled from several individual sources placed around the annular disk as a circular array. The latter approach allows for more flexibility, including the possibility of using an array with more than one type of source. "Collimated" geometry is seldom used unless the source has high-energy components which must be shielded against.

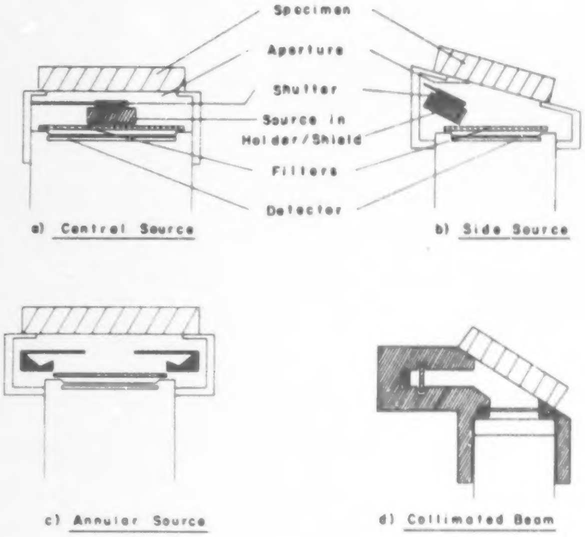


Figure 8. Typical source-specimen-detector arrangements (from Ref. 3).

When a specimen of variable composition or shape is analyzed, uniformity of excitation and response is very important (assuming that the "average" composition is sought). The annular source configuration has the best uniformity for specimens of size comparable with the annular diameter: nearly flat response across the specimen can be achieved within a few percent. Side source geometry is poorer, while central source geometry is the poorest of the arrangements shown, with variations of greater than a factor of two being almost unavoidable.

Encapsulation of sources is an important design consideration: in principle, the source should cover as small an area as possible in the shape of a disk, yet it cannot be made very thick because self-absorption would be a problem. Rhodes (Ref. 3) and Ansell (Ref. 11) discuss these considerations at length.

Use of a secondary target excited by a source can provide a roughly monochromatic x-ray spectrum. For targets of reasonably high atomic number (Z), the monochromaticity is quite good, but the energy of the characteristic K fluorescent radiation increases as atomic number increases, becoming too high for useful analyses of the medium-Z elements when targets of the heaviest elements are used. One advantage of using secondary targets is that they can be switched to obtain excitation x-rays of differing energies. A disadvantage is that to obtain sufficient excitation intensity the primary source must have relatively high activity. Sources and targets have been designed and used as assembled units in order to make them more compact.

B. X-Ray Tube Excitation

X-ray tubes are the most commonly used device for obtaining a source of excitation radiation. The conventional reflection geometry x-ray tube works by accelerating electrons arcoss a voltage difference; when the electrons (energy E) strike the anode, they produce both fluorescent x-rays characteristic of the anode material, and bremsstrahlung with a 1/E spectrum as they decelarate and stop. The beam of x-radiation is brought out of the tube at a large angle from the electron beam direction, hence the term "reflection geometry".

Unfortunately, when a continuous spectrum of energies is used to produce fluorescence in a specimen, difficulties occur in the analysis especially in energy-dispersive analyses: a significant number of the intense low-energy photons incident on the specimen scatter into the detector, producing a large background in the region of the low-intensity x-ray fluorescence peaks. This difficulty has led to the use of more nearly monochromatic excitation sources, one example of which is the use of a transmission-anode x-ray tube, in which the electron beam strikes a very thin anode in which both bremsstrahlung and fluorescence occur. The anode material is chosen to produce characteristic fluorescent radiation of the desired energy and the accelerating potential is selected to maximize the ratio of characteristic x-radiation to bremsstrahlung. Under optimum conditions, the thin anode transmits the characteristic line while filtering out much of the low-energy bremmstrahlung.

Another method is the use of a secondary fluorescent target together with a conventional x-ray tube, to produce more nearly monoenergetic x-radiation which is characteristic of the secondary target. This is a more versatile approach, since the target material and tube potential can both be adjusted to produce a range of excitation energies suitable for the particular problem at hand.

C. Filters for Tuning the Excitation Energy

The use of filters to alter the photon energy distribution of the fluorescent radiation can provide significant improvements in some situations. This technique is called the "balanced filter" method, and is exemplified by the following discussion (from Ref. 3).

Figure 9 (Ref. 3) shows the x-ray transmission probability through a nickel filter of thickness 10.5 mg/cm^2, and a copper filter of 9.8 mg/cm^2. The thicknesses are chosen so that the absorption curves match almost exactly except in the narrow "pass band" between the Ni and Cu absorption edges. By operating the instrumentation with first one and then the other filter, a subtraction may be made which is sensitive only to the pass band. Note that the zinc K_α line is within the pass band, and can therefore be separated from other possible interferences, except for the copper K_β line, which is shown in Figure 9 as being just inside the band.

This technique can be made very selective, with limitations mainly due to sensitivity difficulties because of the statistical uncertainties from subtracting large comparable numbers to obtain a small difference. The operating time needed to obtain high sensitivity is long, making this method uncompetitive when multi-element trace analyses must be performed. However, this method is widely used in field situations, where portable analyzers are advantageous.

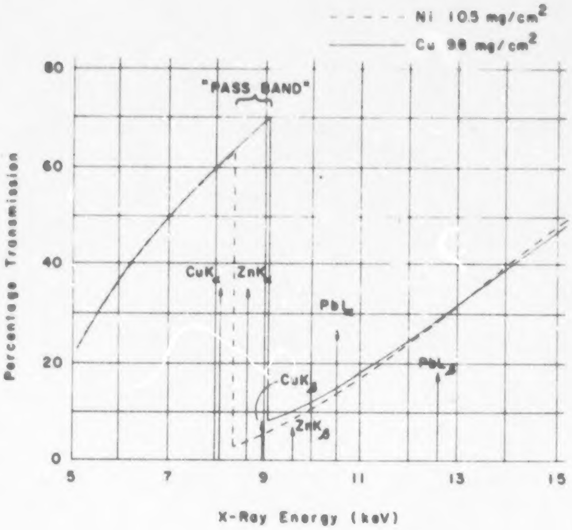


Figure 9. X-ray transmission through balanced filters of copper and nickel (from Ref. 3).

D. Charged Particle Excitation

The use of charged particles as the exciting means in x-ray fluorescence energy-dispersive analysis has received considerable attention. (The term "fluorescence" is not strictly applicable to particle excitation, but will be used here in analogy to the photon-excitation methods.) Among possible particle types are electrons, protons, and alpha particles. However, electrons have the serious difficulty that they produce bremsstrahlung in the specimen, the intensity of which is exceedingly high compared to that of the fluorescence x-rays. Hence, they do not provide competitive sensitivity, and are seldom used for trace-element analysis of the type considered here. Scanning electron microscopy with x-ray analysis is primarily useful for examining detailed structure in specimens rather than for trace analysis.

Protons or alpha particles in the few-MeV region are often used for trace element analysis. However, again the production of electrons as the beam traverses the specimen is a problem. These electrons produce bremsstrahlung as they decelerate, and this is an important background for the fluorescent x-radiation. While the excitation cross-sections are high, the backgrounds can also be relatively high, unless very thin specimens are employed.

A recent paper by Folkmann et al. (Ref. 12) has thorough calculations of the various contributions to the background using a proton-induced energy-dispersive system. Some of the results are shown in Figure 10, in which are plotted the fractional concentration as a function of atomic number Z at which the K x-ray signal is as intense as the background, using a carbon matrix. From this figure and others in Reference 12, it appears that using few-MeV protons, sensitivities in the parts-per-million range are achievable in optimum situations. This is comparable to that achievable with photon excitation systems. A good comparison of sensitivities has been given by Goulding and Jaklevic (Ref. 1). Cooper (Ref. 13) has reached similar conclusions, but he concludes that alpha-particle excitation has intrinsic sensitivities somewhat poorer than those achievable with protons. More recent work by Cahill et al. (Ref. 14) indicates that protons at 4 MeV and alphas at 16 MeV, which have nearly equal velocities, are reasonably comparable insofar as attainable sensitivity is concerned.

However, there are important difficulties with particle excitation. One important limitation is that few-MeV protons and alphas have such low residual range that they can only be used for very thin specimens (less than a few mg/cm^2 in thickness), unless non-uniform irradiation near the surface is acceptable. Also, high intensity particle beams, when focussed well, may produce enough intense local heating to burn a hole in a thin specimen such as an air filter; but at lower intensities analysis time becomes long and many accelerators are difficult to control well. Finally, there are often problems with attaining uniform irradiation of large-area samples with a particle beam of small cross-section. (On the other hand, the technique is particularly applicable to samples of very small diameter, since the particle beams can usually be very well focussed.)

V. ENERGY SELECTIVE SYSTEMS

Prior to the mid-twentieth century a number of energy-selective systems were in use, but none of them was adequate for rapid, multi-element trace x-ray fluorescent spectroscopy. This was particularly true for the minute concentrations that are involved in environmental contamination analysis, which were usually analyzed with wavelength-selective systems until about 15 years ago. The advent of the semiconductor radiation detector in the mid-1960's changed all this, and revolutionized the field of x-ray fluorescence analysis. Such devices have now become widely used as sensitive high-resolution x-ray detectors.

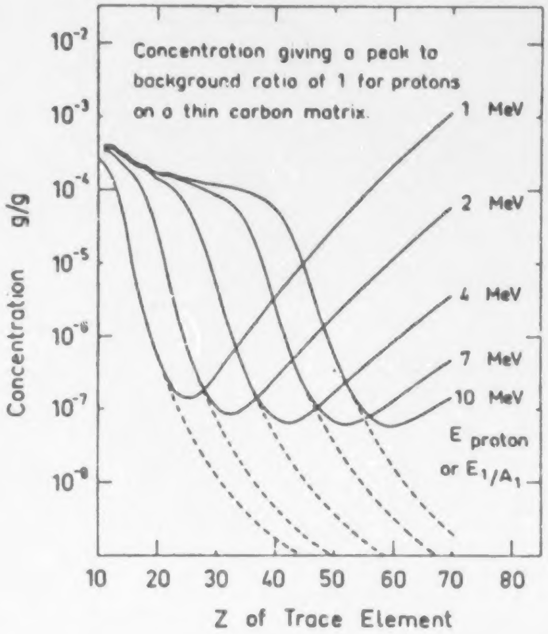


Figure 10. Calculated concentration for which the K x-ray in a Si(Li) detector is as intense as the background bremsstrahlung from secondary electrons and protons (from Ref. 12).

A. Silicon Semiconductor Detectors

Silicon semiconductor detectors, lithium-drifted to compensate for electrically active impurity centers, are now the most widely used high-resolution detectors for x-rays.

Figure 6 above has already introduced the fact that the resolution obtainable with these detector systems is very good. Among their other properties are their stability, high-count-rate capability, small size, and low background counting rates. Since 1969 (the date of Figure 6), improvements have brought the resolution down to the region of about 100 eV (full width half maximum, FWHM), which allows separation of element pairs as low in the periodic table as carbon/nitrogen.

Two recent improvements have been in preamplifier design and performance, and in detector design and electric field shaping to improve charge collection efficiency.

The early silicon semiconductors had resolution in the 2 keV range (FWHM), limited primarily by the properties of the preamplifiers. The introduction in 1965 of low noise field effect transistors (FET's) operated at low temperatures improved the resolutions to the range just below 1 keV. Gradual advances in manufacturing methods and optimization of operating conditions brought even more improvements, with resolutions of about 250 to 300 eV limited by the feedback resistor to the preamplifier. Recent developments have improved the resolution still further to the 100 eV range. There have been several approaches, one of which, developed by Goulding's group, achieves improved performance by replacing the feedback resistor with light coupling from a light-emitting diode to the photosensitive drain-gate FET junction (Ref. 15). Still further improvement in the performance at high counting rates was achieved by introducing a pulse-light feedback technique, thereby keeping the preamplifier in the proper range and preventing it from drifting into a non-linear range at high rates. This has been thoroughly described by Goulding et al. (Ref. 1). With a rejection system to eliminate events which occur while an event is already being processed, this system can achieve excellent resolution and can maintain it up to random counting rates in the region of 20,000 counts per second.

Improvements in charge collection efficiency have been equally important in reducing the background caused by electrical charge pulses in which all of the liberated charge has not been collected (see Fig. 7). The common top-hat, planar and grooved geometries (Fig. 11, from Ref. 16) suffer because charge deposited in some parts of the detector volume is incompletely collected, being collected by the surface n-type layer rather than by the bulk field. The only geometry which almost completely avoids this is that in which a guard ring is provided (Fig. 12). Such a ring improves the shape of the internal electrical field lines. However, some events still have incomplete charge collection if charge is liberated near the boundary; hence a guard ring with a veto feature (Fig. 12,

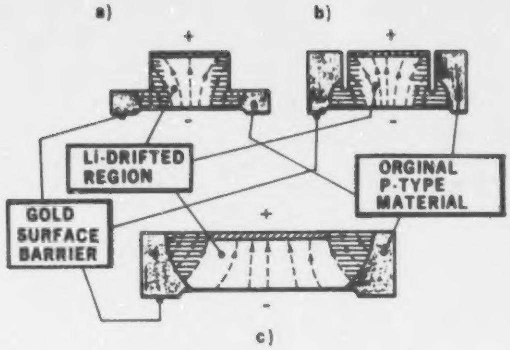


Figure 11. Types of detector configuration used in x-ray spectrometers:

a) Top-hat detector

b) Grooved detector

c) Planar detector (from Ref. 16).

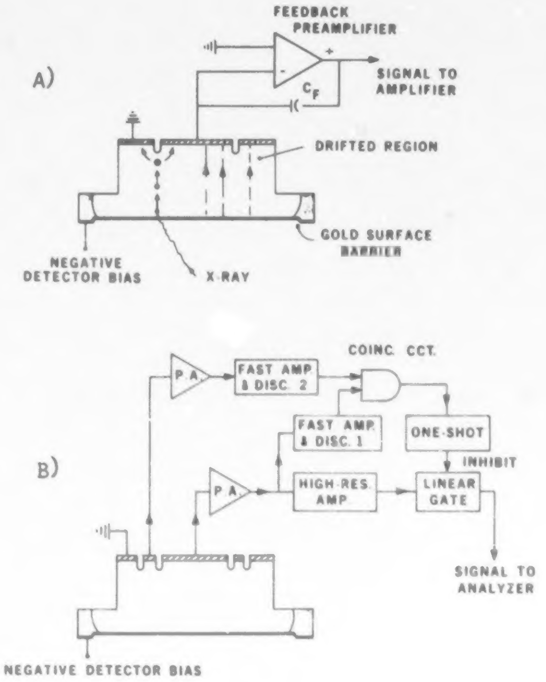


Figure 12. Guard-ring detectors. (a) Simple guard-ring approach showing the mechanism for degraded pulses. (b) Double guard-ring detector with pulse-reject circuitry to remove degraded pulses (from Ref. 16).

Ref. 16) will yield still better performance: events are rejected whenever significant charge is collected in the region outside the central groove. With this system, events with incomplete charge collection are dramatically reduced in number. A double guard ring, like that shown in Fig. 12, provides even better performance by decreasing the area in which the veto pulses are generated and hence the noise in the veto electronic system. Reductions in background of factors as high as 40 when compared with some top-hat detectors have been reported (Ref. 1), employing cadmium x-rays on a lucite test specimen. Similar results can be achieved with collimation of the excitation radiation, although this usually involves substantial losses in excitation intensity and hence in sensitivity. This has been well discussed by Woldseth (Ref. 5).

The ultimate physical effects which produce an irreducible background beneath the fluorescent peaks are due mainly to two effects: low-energy bremsstrahlung emitted by Compton electrons in the specimens, and photoelectron escape from the surface of the detector. Actual background performance today is in the range of about one background photon per 200 eV energy interval, for every 10^4 photons in the scattered peak. This is about one to two orders-of-magnitude above the ultimate limits just discussed. The mechanisms which prevent achieving the irreducible-background situations are still not completely understood, but research is now in progress to clarify the situation (Ref. 17).

B. Other Energy-Dispersive Detectors

Semiconductor detectors based on germanium are possible close competitors to silicon-based detectors. The high atomic number of germanium means that it has a higher absorption coefficient for x-rays. This is particularly important for capturing higher-energy photons, unimportant at lower energies. Germanium's lower band-gap energy means that more charge carriers are freed per unit energy lost by the x-ray photon; thus, other things being equal, it will have better energy resolution. The lithium-drifted germanium detectors must be stored as well as operated at low temperatures, a disadvantage which is overcome by the recently-available intrinsic germanium detector systems. Intrinsic germanium detectors suffer from high leakage currents. However, an important disadvantage for trace analysis. Also, at energies above about 10 keV, the spectrum from a germanium detector is complicated by the presence of the 'escape peak', due to germanium K x-rays escaping from the detector surfaces and hence degrading the full-energy photopeak.

Figure 6 above indicated that the resolution of semiconductor detectors far exceeds that of the energy-dispersive detectors not based on semiconductors. For example, gas proportional counters have about one order-of-magnitude poorer resolution than Si(Li) detectors over most of the interesting energy range, while sodium-iodide scintillation counters have perhaps still another factor of 3 poorer resolution. Because of this, these instruments cannot compete with the semiconductor detectors for most trace-element applications: they are generally unable to differentiate between adjacent elements in the periodic table, and have significantly poorer sensitivity because the background region beneath a fluorescent peak of greater width is larger than that beneath the narrower Si(Li) peak. The gas proportional and sodium iodide systems can seldom obtain detection limits below about 50 ppm for analyses in which interferences are known to be unimportant (Ref. 3): in favorable cases, as low as 10 ppm can sometimes be obtained.

C. Si(Li)-Detector Systems Performance

The discussion above has indicated that silicon semiconductor detectors, used with nearly monoenergetic excitation radiation from either a radioactive source or an x-ray tube, seem to provide the best combination of parameters for sensitive x-ray fluorescence analysis of trace elements by the energy-dispersive technique, especially for medium-Z to high-Z elements.

The performance of actual systems is not easy to summarize. The basic goals of the systems under discussion are sensitivity, accuracy, lack of interference, and multi-element capability. Systems of similar conceptual design and even similar hardware features can be designed and operated to optimize some of these parameters at the sacrifice of others but no system has been designed which optimizes all. This makes any attempt to summarize performance specifications difficult. Perhaps the best way to overcome this is to cite a few typical performance data for actual systems, because among other things the systems in use may operate under differing constraints: for example, a system which seeks the ultimate in sensitivity is operated quite differently from one which must routinely analyze a certain number of samples per day within fixed cost limits.

An example of a system developed for rapid, many-sample analysis of a large number of elements on air filters is the spectrometer developed by Goulding and Jaklevic for the

U.S. Environmental Protection Agency (Ref. 18). The goal of this system is the capability of rapidly measuring important elements collected on air particulate filters, at the level of a few ng/cm² on the filters, corresponding to several tens of ng/m³ in the sampled air (two hours of collection time at about 50 liters/minute).

The system uses three secondary-fluorescent targets and a variable-voltage x-ray tube in order to cover a sufficiently wide range of elements. The targets are Cu, Mo, and Tb, with principal x-ray lines at energies of 8.0, 17.4, and 44.0 keV, respectively. This is necessary because (as has been pointed out earlier) the probability of excitation falls rapidly as the difference between excitation energy and x-ray absorption edge increases. Several small effects decrease actual sensitivity for elements near the cutoff, with the result shown in Fig. 13 (Ref. 18) which gives the actual relative efficiency curves for the three fluorescers. These translate into elemental detection sensitivity curves in Fig. 14, where 3σ above background is plotted, and three 5-minute analyses are performed, one for each fluorescer. (The ordinate shows ng/m³ of air; to convert to ng/cm² on the filter, multiply by 0.8 m³/cm²).

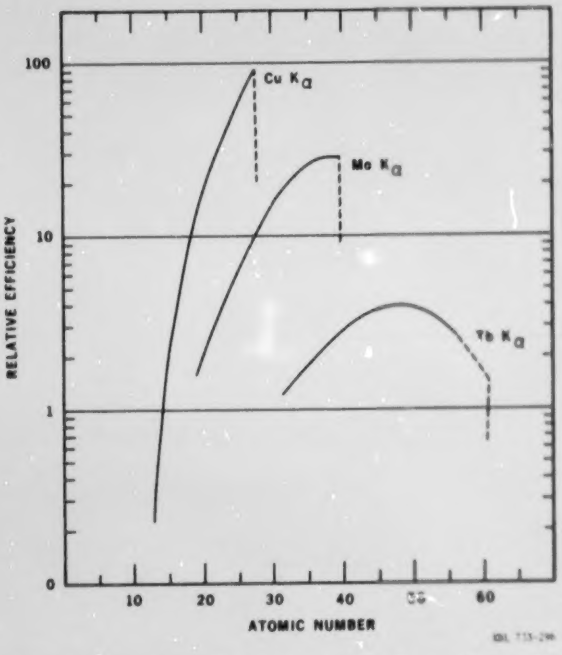


Figure 13. Relative efficiency curves for three fluorescers (see text) (from Ref. 18).

Also shown is a point for lead, whose L_β x-ray at 12.61 keV provides the sensitivity indicated. The lowest element detectable with reasonably good performance in this system is aluminum (Z = 13).

This system has been developed with attention to a large number of engineering details, to improve reliability and sensitivity. It employs a double-guard-ring cooled Si(Li) detector, and incorporates an automatic data analysis system in which a small computer performs pulse-height analysis, unfolding of the accumulated spectrum, printing out of the elemental determinations, controlling of the time sequence of sample changing and sample irradiation with successive fluorescers, controlling x-ray anode voltage and current, and performing many other bookkeeping tasks.

The analytical sensitivity of the system just described can be improved by using longer data analysis times, at least up to some limit.

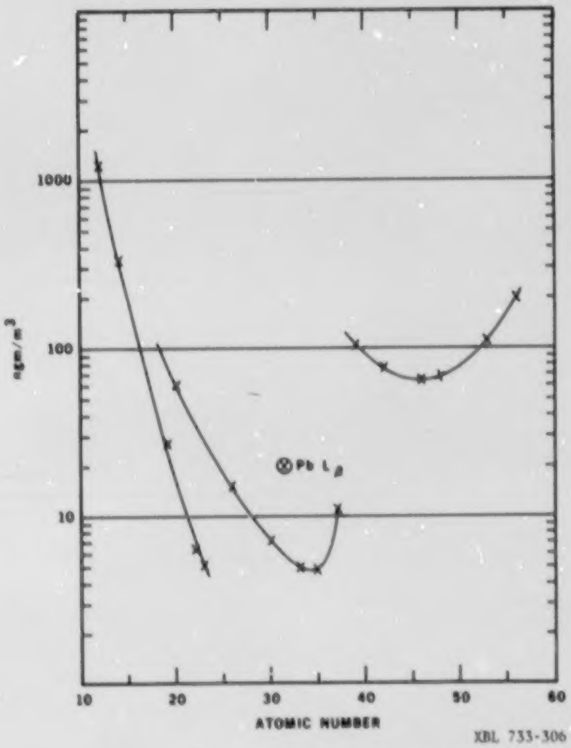


Figure 14. Elemental detection sensitivity curves for three fluorescers (two hour sample collection time, five minute analysis time on each fluorescer) (from Ref. 18).

The improvement can be expected to be inversely proportional to the square root of analysis time, $\sim\sqrt{t}$ until other systematic effects besides statistics above background become important. Using a system with many similar features, for example, Giauque et al. (Ref. 2, 19) have achieved detection limits 3 to 5 times smaller by counting longer and using slightly more sophisticated analytical methods.

Another system whose performance has been well documented is the radioactive source-excitation system described by Rhodes et al. (Ref. 20). Three annular radioactive sources are used to cover three energy ranges:

^{55}Fe,	120 mCi,	5.9 keV	(Mn $K_{x\text{-rays}}$)
^{238}Pu,	400 mCi,	12 to 17 keV	(U $L_{x\text{-rays}}$)
^{109}Cd,	12 mCi,	22.2 keV	(Ag $K_{x\text{-rays}}$)

The Si(Li) detector has resolution of 180 eV (FWHM) at 5.9 keV, and the system includes a minicomputer with automatic operation of the sample and source changer and the spectrometer system. The limit of sensitivity is given by the strengths of the sources used, the backgrounds due to detector charge collection problems (which can be improved using better semiconductor detector systems) and the deadtime limitations in the electronic circuitry. The absolute calibration of the system is achieved by reference to an americium-241 source (59.6 keV gammas, 14 to 17 keV neptunium-237 x-rays), which is counted simultaneously with the fluorescence spectrum. With analysis times of 10 minutes for each source exciter, the detection limits in ng/cm^2 (3σ above background) of this system appear to be about a factor of 2 to 5 worse than those shown in Fig. 14 for the system of Goulding et al. (Ref. 18). Both systems are sufficiently sensitive to measure samples from air filters, especially when operated with air sampled at about 4 m^3/cm^2, which is 5 times more than that sampled by Goulding in Ref. 18.

An unusual system described by Sparks et al. (Ref. 21) uses a graphite diffraction element to achieve a monochromatic x-ray excitation beam. The system is shown schematically in Fig. 15. The energy spectrum from a molybdenum-target x-ray tube at 40 keV is shown in Fig. 16, before and after diffraction from the (002) basal planes of graphite. Using this system and a Si(Li) detector, detection limits in the parts-per-million region are claimed, although not discussed quantitatively. This system employs a collimator rather than a guard ring to decrease the backgrounds beneath the fluorescent peaks.

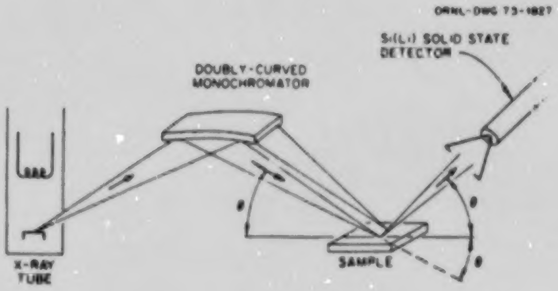


Figure 15. Arrangement using a primary beam monochromator to selcct a monoenergetic x-ray source to excite characteristic x-rays for fluorescent analysis. Solid state detector provides the energy resolution for identifying the fluorescent energies from the sample (from Ref. 21).

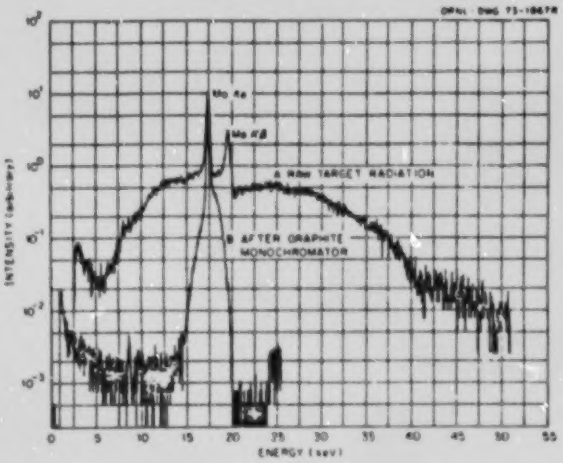


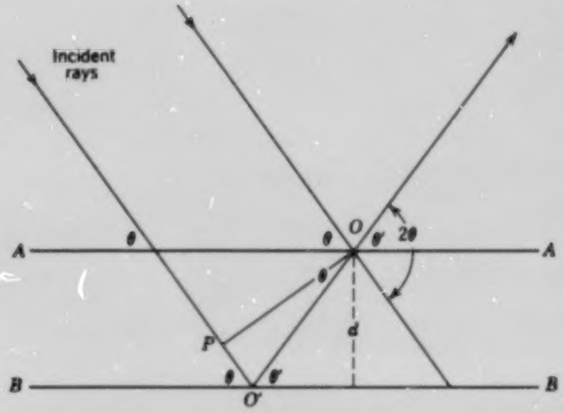
Figure 16. Energy spectrum from a molybdenum-target x-ray tube operated at 40 keV full-wave rectification. Curve A is before and B is after monochromation by diffraction from the (002) basal planes of graphite. Both intensities were attenuated by 3-mm-thick polystyrene and recorded by use of a Si(Li) detector (from Ref. 21).

D. Wavelength Dispersive Systems

The wavelength-dispersive technique derives its name from the fact that the analysis of the x-ray beam occurs by "Bragg reflection" (actually diffraction) of the x-ray waves from a crystal or other planar-geometry object. The phenomenon, long the most important method for x-ray analysis, relies on the fact that crystals (or other similar wavelength analyzers) possess planes of symmetry with regular spacings. Essentially, the crystal acts as an x-ray grating composed of parallel planes, from which photons can be coherently scattered so that they are in phase at certain angles. They reinforce each other, producing a diffraction pattern. This "Bragg diffraction" is often mis-named "Bragg reflection". Although this phenomenon and its explanation are quite well known, we will give a brief description here.

We quote from Liebhafsky et al. (Ref. 7),

> "The conditions for Bragg reflection are diagrammed in Fig. 17 where AA' and BB' are the traces of successive Bragg planes, d their distance apart, and θ the glancing angle of the incident x-ray beam on these planes. Bragg reflection occurs when a wave scattered at θ' can reinforce an identical wave scattered at θ."



$$OO' = \frac{d}{\sin\theta}$$

$$O'P = OO' \cos(180^\circ - 2\theta) = -OO' \cos 2\theta = -\frac{d \cos 2\theta}{\sin\theta}$$

$$OO' + O'P = n\lambda = d\left[\frac{1 - \cos 2\theta}{\sin\theta}\right] = d\left[\frac{1 - 1 + 2\sin^2\theta}{\sin\theta}\right]$$

$$n\lambda = 2d \sin\theta$$

Figure 17. Simplified derivation of Bragg's law (from Ref. 7).

Bragg's law can be derived easily from Fig. 17 and states that the angle θ at which the reinforcement of phase occurs is given by

$$\sin\theta = \frac{n\lambda}{2d} ,$$

where λ is the wavelength and n is any positive integer, termed the order of the reflection.

Though termed "wavelength dispersive", since the wavelength is conceptually the parameter involved, the system is of course also energy dispersive, because energy E and wavelength λ are related by the equation $E = hc/\lambda$ (h is Planck's constant and c is the velocity of light).

The wavelength resolution of Bragg diffraction devices is very good. In many practical instruments it is limited more than anything else by the need to collimate a divergent beam into a roughly parallel one with a finite aperture. Naturally, when such angular collimation is used, there is a decrease in intensity as a trade-off for increased wavelength resolution. The resolution of typical systems as a function of energy has already been displayed above in Fig. 6, where it is compared with the resolution attainable with various energy-dispersive systems. Fig. 6 reveals that for long-wavelength low-energy x-rays the resolution of Bragg-diffraction instruments is superior to that of any other system.

The wavelength-dispersive technique has been specially adapted to apply to trace x-ray fluorescence analysis. Consider, for example, the excitation of fluorescent x-radiation by a monoenergetic x-ray source. The energy spectrum produced in the specimen by such exciting radiation has already been shown schematically in Fig. 7 above. The task of the detection system is to measure the intensities of the various individual fluorescent lines while rejecting backgrounds such as the much more intense (and higher-energy) scattered photons. These backgrounds, while high, are significantly less troublesome than those in energy-dispersive systems. In principle, by varying θ, a single crystal can analyze all wavelengths such that $\lambda > d$. In practice, limitations exist from geometrical considerations; for example, wavelengths a factor of 2 apart (λ and 2λ, say) will in general both be enhanced at the same angle θ; in practice, they can be separated either by a measurement at some different θ' where the shorter wavelength alone is enhanced, or by using a sinusoidal potentiometer with which a given order of reflection is automatically selected. Another practical consideration is that in order to resolve two lines which differ in λ by, say 0.5%, two diffracted rays must be separately detected at angles whose sines differ by that same fraction, 0.5%:

$$\frac{\lambda'}{\lambda} = 1.005 = \frac{(\sin\theta)'}{\sin\theta}$$

It turns out that profile shape is an even more important consideration, and this is determined mainly by the collimation geometry. These effects produce extreme constraints on the geometry, and the easiest solution was arrived at early in the history of this field, namely using a narrow slit at both x-ray source and detector, and rotating the analyzing detector (and its slit) twice as fast as the crystal. This is shown schematically in Fig. 18 (Ref. 7), in which an early rotating spectrometer is displayed.

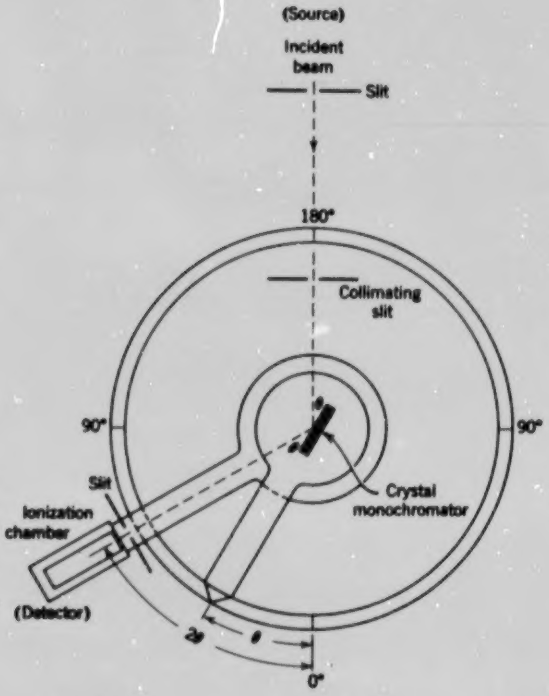


Figure 18. Schematic diagram of the Bragg spectrometer. To scan a wavelength range, the crystal is rotated at angular velocity dθ/dt, and the detector at angular velocity d(2θ)/dt (from Ref. 7)

A difficulty with this system, of course, is long analysis time. Unless multi-crystal systems with many parallel channels are used, each wavelength region must be scanned in sequence, so that a measurement over a wide wavelength range takes considerable time. Another difficulty is that each particular crystal type is only useful over a limited wavelength range because of its interplanar spacing d. (This is also an advantage in that the angular dispersion can be selected.) This is shown in Fig. 19 (Ref. 7), where the wavelength ranges of 14 different reflectors are displayed, for the angular range (2 θ) from 8° to 145°. Table 2 (Ref. 7) explains the compositions of the Bragg diffractors shown in Fig. 19, along with some remarks on their performance.

The advanced x-ray fluorescence systems nearly all contain multiple reflectors, each "tuned" geometrically to one (or a few) particular wavelength channel(s). Each spectrometer channel can in this manner be optimized for the particular element being measured, including not only choice of best crystal but also best geometrical layout, best divergence (acceptance), and best detector set-up. In general, the detectors used in such systems are either flow-through gas proportional counters or scintillation counters, which possess high detection efficiency and large sensitive area.

Details on choice of crystals and the relative advantage of flat, curved, and other types of crystals are discussed in a number of standard works, for example, Liebhafsky et al. (Ref. 7). Here we will not delve into these details, nor into many of the other factors in the lore of the crystal-diffraction spectroscopist. Instead, we will concentrate on the performance specifications for fluorescence analysis systems measuring environmental samples. For these performance specifications, we rely on the work of Birks et al. (Ref. 22, 23, 24) as typical of what can be obtained.

The first general comment is that quite low detection limits, in the range of one to a few tens of nanograms/cm^2, can be achieved (with analysis times of a few minutes) for elements deposited on a thin substrate, say, a cellulose air filter. The detection limits vary smoothly from one element to the next in the periodic table, except when a jump from K to L lines occurs. The use of high-powered x-ray tubes is usually called for, and except in unusual situations radioactive

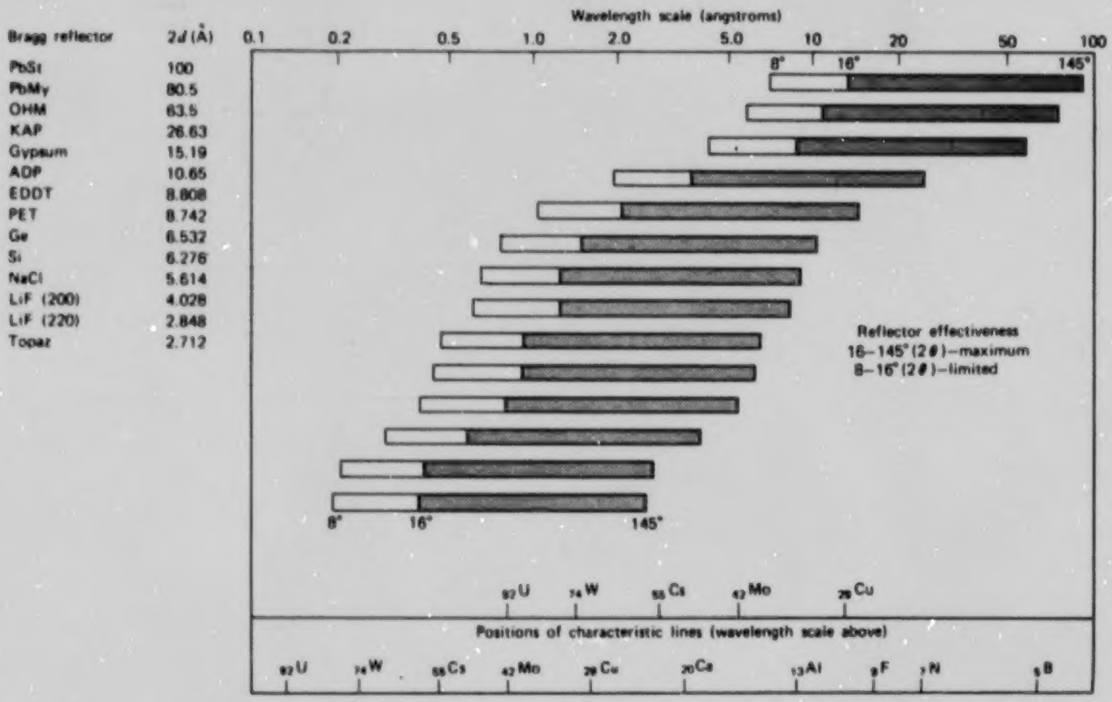


Figure 19. Flat Bragg reflectors for x-ray emission spectrography; spacings and useful ranges (from Ref. 7).

TABLE 2.

Further Information for Flat Bragg Reflectors for X-Ray Emission Spectrography

(from Ref. 7)

Bragg Reflector	Name	Remarks
PbSt	Lead stearate	Langmuir-Blodgett grating
PbMy	Lead myristate	All following reflectors are crystals
OHM	Octadecyl hydrogen maleate	Good for determining carbon
KAP	Potassium acid (hydrogen) phosphate	Preferred for determining F or Na
Gypsum	Calcium sulfate dihydrate	May effloresce. Store properly
ADP	Ammonium dihydrogen phosphate	Low intensity
EDDT	Ethylenediamine ditartrate	Low intensity
PET	Pentaerythritol	Higher intensity than the preceding two
Ge	Germanium	Both elements: even orders missing
Si	Silicon	in reflection. Intensity comparable
NaCl	Sodium chloride	Useful but hygroscopic. Store properly
LiF (200)	Lithium fluoride. Note Miller indices	Best general-purpose crystal
LiF (220)	Lithium fluoride. Note Miller indices	Good intensity. High resolution
Topaz	Aluminum fluosilicate (hydrated)	Best resolution

sources and secondary-fluorescer devices are ruled out. Because Bragg diffraction is not perfectly selective, there is some background at any given angle θ from x-rays whose main diffractive peaks are at other angles. This background, which can be largely removed by pulse-height selection, is one of the intrinsic limitations to the technique. Another major limitation is the coherent and incoherent scattering of the primary radiation by the atoms in the specimen.

Birks and Gilfrich (Ref. 24) examined four commercial multi-crystal instruments, and found detection limits for many important elements in the 1 to 10 ng/cm^2 range. Apparently, a key difficulty with one of the instruments is that it does not employ pulse-height discriminators on all detector channels, and is thus not always able to discriminate against higher-order diffraction of shorter wavelengths, or against other unwanted radiation. Pulse height analysis would seem to be an important feature. It appears that neither the flat nor the curved crystal geometry offers any unusual advantage over the other type.

The various commercial systems studied can analyze 14 to 28 elements simultaneously, from Na (detection limit ∿ 100 ng/cm^2) and Al (∿ few ng/cm^2) to Cu and Zn (∿ few tens of ng/cm^2) and Pb (also ∿ few tens of ng/cm^2). Table 3, taken from Birks and Gilfrich (Ref. 24), indicates the approximate detection limits for several important elements. The systems are intrinsically limited: for a given sample and set-up the entire fluorescent x-ray spectrum is not observed, since it is necessary to choose beforehand the elements (lines) to be measured. This is perhaps a disadvantage over the energy-dispersive systems, compensated for by the high specificity of the analyses which are performed. Another compensation is that elements of low atomic number are more easily resolved and analyzed with wavelength-dispersive systems, often with much better sensitivities. In the region of the transition elements of the periodic table, the sensitivities are not as good, however.

The fact that sensitivity may be excellent for these systems is not sufficient by itself to recommend them for routine use

TABLE 3.

3σ Detection Limits: ng/cm^2 on Filter Paper (100 sec. Measurement)

Four Commercial Instruments Were Evaluated. Each "x" Corresponds to the Performance of One of the Instruments. (from Ref. 24)

	1 - 5	5 - 10	10 - 50	50 - 200	200 - 500
Na				xx	x
Mg			xxx	x	
Al	xx	xx			
Si	xx	xx			
S	xx	xx			
Cl		xx	x		
K	xx	x			
Ca	xx	x			
V		x	x		
Fe			x	xx	
Co			xx		
Ni			xxxx		
Cu			x	xxx	
Zn			xx	x	
As(K_β)				x	
Cd(L_α)	x			x	
Pb(L_α)			xx		

in trace element analysis. There are intrinsic difficulties with precision, which can only be overcome by careful attention to the details of a particular system.

VI. COMPARISONS, SUMMARY, AND CONCLUSIONS

The discussions above have indicated that both energy-dispersive and wavelength dispersive systems, when used with photon excitation, have sensitivities sufficient to determine a large number of trace elements at concentrations in the range of 1 to 100 ng/cm^2, on a thin sample and with a few minutes' counting time. The proton-induced energy-dispersive technique has comparable intrinsic sensitivities while alpha excitation yields somewhat poorer sensitivities.

Other considerations besides sensitivity must be considered, however. For example, the detailed understanding of the many factors which Giauque et al. (Ref. 2) have brought to the photon-excited energy-dispersive technique allows very high precision. The particle-excitation systems have not yet been so fully understood. This is complemented by an ease of operation and low unit cost which probably make photon excitation the analysis method of choice for most environmental samples.

One useful comparison of some of the energy-dispersive systems has recently been performed by Cooper (Ref. 13). In Figures 20 and 21, taken from Cooper, spectra are displayed for seven different techniques, all analyzing the same specimen, a National Bureau of Standards standard orchard leaf (Ref. 25). This standard material contains a few ppm of each of the several elements displayed in the figures.

The figures referred to reveal much in themselves. Detailed signal-to-noise studies indicate that within factors of 2 to 4, all of these systems except the alpha excitation technique offer comparable sensitivity. (The 75-mCi ^{109}Cd source and the 100-mCi ^{55}Fe source each require considerably longer counting times to achieve comparable statistical significance, but this is easily remedied by use of stronger sources.) Among the energy-dispersive systems, the choice of one excitation method over another ultimately depends on precision desired, costs, and convenience. Improvements in incomplete-charge-collection difficulties in silicon detectors will benefit the photon-excitation systems most. Other improvements in silicon-detector technology will probably benefit all of these systems in comparable ways.

The comparison between the better energy-dispersive systems and their wavelength-dispersive competitors has not been well explored as yet. Birks' study (Ref. 22, 23, 24) indicates that sensitivities may be comparable to those found in Cooper's study (Ref. 13, 26). At low atomic numbers, the crystal-diffraction systems have an apparent intrinsic advantage, because of their excellent low-energy resolution. However, their ability to analyze a variety of samples with a good precision has not been demonstrated, and the need to calibrate each channel separately is a difficulty compared to the energy-dispersive systems with their slowly varying Z-dependent sensitivity. Recent work by Goulding and his group has been aimed at improving the energy-resolution performance of the photon-excited energy-dispersive systems for the lowest atomic numbers (Ref. 17). This may narrow the competitive advantage in sensitivity of the wavelength-dispersive systems even in this regime.

In conclusion, there seem to be several x-ray fluorescence techniques which can perform analyses of trace elements in environmental samples at concentrations down to the range of a few ppm (equivalent to a few ng/cm^2). Further development of these techniques probably holds out the promise of still further improvements in performance, particularly regarding resolution, counting-rate abilities, and background reduction. Because the x-ray fluorescence methods have a slowly-varying dependence of sensitivity with Z, and because they can cover a wide range of Z without gaps, they offer particular advantages to the analyst.

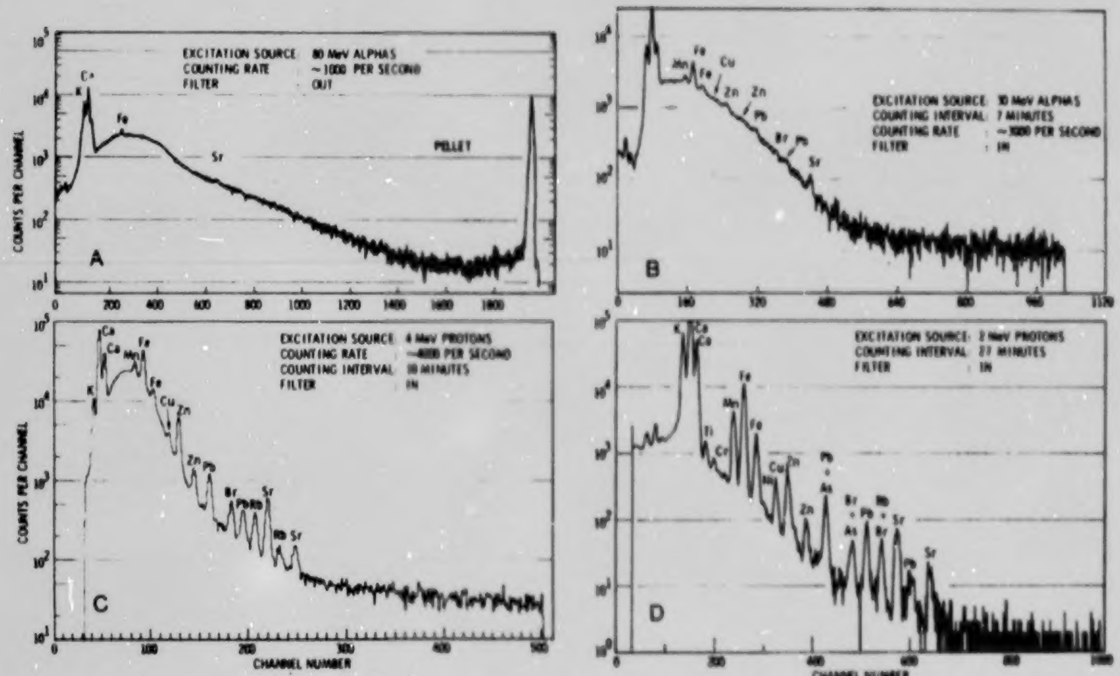


Figure 20. X-ray spectra of the elements contained in NBS standard orchard leaf as excited by (a) 80 MeV alphas, (b) 30 MeV alphas, (c) 4 MeV protons, and (d) 2 MeV protons (from Ref. 13).

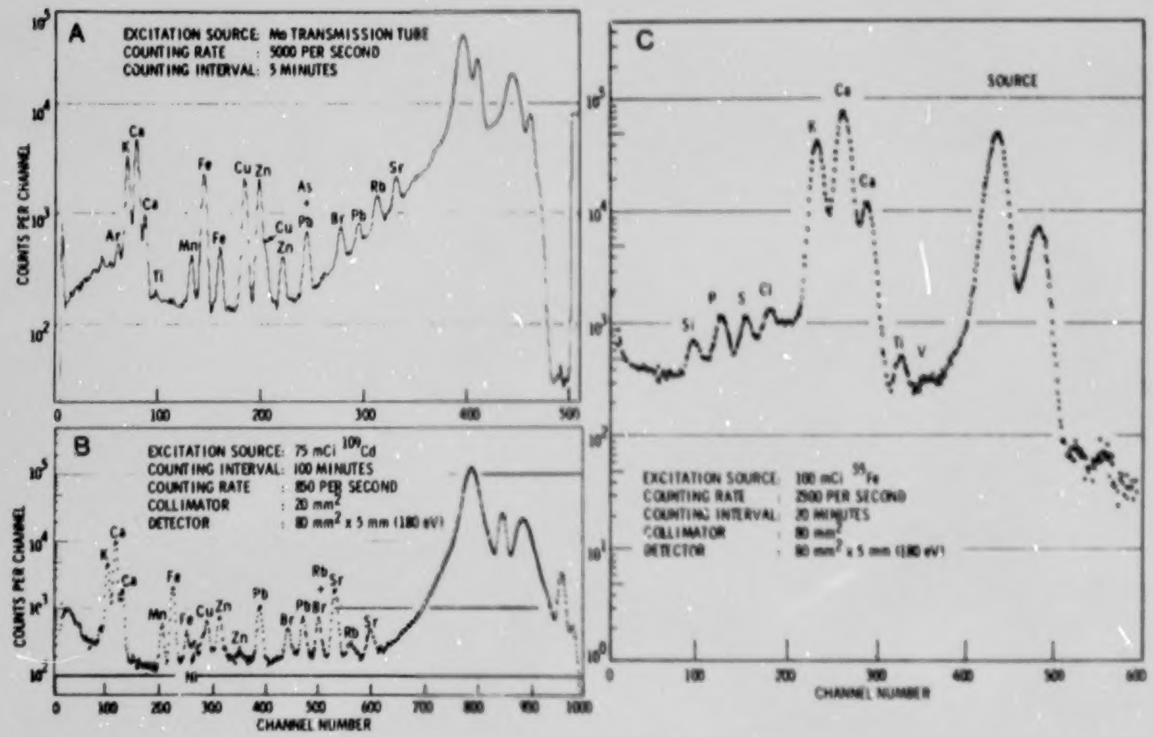


Figure 21. X-ray spectra of the elements contained in NBS standard orchard leaf as excited by (a) Mo transmission tube, (b) ^{109}Cd radioisotopic source and (c) ^{55}Fe radioisotopic source (from Ref. 13).

VII. ACKNOWLEDGMENT

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F.S. Goulding,
Lawrence Berkeley Laboratory

J.M. Jaklevic,
Lawrence Berkeley Laboratory

R. Jenkins,
Philips Electronic Instruments

J.R. Rhodes,
Columbia Scientific Industries

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IX. COMMERCIALLY AVAILABLE INSTRUMENTATION

Instead of a compilation of Instrument Notes we list here those commercial firms which are listed under "X-Ray Fluorescence Equipment" in the 1974 Science Magazine "Guide to Scientific Instruments" (Vol. 186, No. 4165A, 26 November 1974):

ANGSTROM, Box 248, Belleville, MI 48111.
APPLIED RESEARCH LABS, Box 129, Sunland, CA 91040.
BLAKE INDUSTRIES, Box 464, Springfield, NJ 07081.
CANBERRA INDUSTRIES, 45 Gracey Ave., Meriden, CT 06450.
CHEMPLEX INDUSTRIES, 34 Bradley Rd., Scarsdale, NY 10583.
COLUMBIA SCIENTIFIC INDUSTRIES, Box 6190, Austin TX 78762.
DIANO-INDUSTRIAL X-RAY, 2 Lowell Ave., Winchester, MA 01890.
EG&G/ORTEC, 500 Midland Rd., Oak Ridge, TN 37830.
EDAX INTERNATIONAL, Box 135, Prarie View, IL 60069.
FINNIGAN, 845 W. Maude Ave., Sunnyvale, CA 94086.
INAX INSTRUMENTS, Box 6044-Stn. J, Ottawa, Ontario, Canada K2A 1T1.
LABTEST EQUIPMENT, 11828 La Grange Ave., Los Angeles, CA 90025.
NUCLEAR EQUIPMENT, 931 Terminal Way, San Carlos, CA 94070.
NUCLEAR SOURCES & SERVICES, Box 14023, Houston, TX 77021.
NUCLEONIC DATA SYSTEMS, 1821 McGaw Ave., Irvine, CA 92705.
PHILIPS ELECTRONIC, 750 S. Fulton Ave., Mount Vernon, NY 10550.
PITCHFORD INDUSTRIES, 1901 Painters Run Rd., Pittsburgh, PA 15241.
PRINCETON GAMMA-TECH, Box 641, Princeton, NJ 08540.
RIGAKU/USA, Lakeside Office Pk., Wakefield, MA 01880.
SIEMENS, 186 Wood Ave., Iselin, NJ 08830.
TEXAS NUCLEAR, Box 9267, Austin, TX 78766.
TRACOR NORTHERN, 2551 W. Beltline Hwy., Middleton, WI 53562.
UNITED STATES RADIUM, 1425 - 37th St., Brooklyn, NY 11218.

C.4. CONTENTS

FOR

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NEUTRON ACTIVATION ANALYSIS

The technique of neutron activation analysis for elemental composition has advanced so much in recent years that many laboratories are now carrying out routine analytical programs on large numbers of environmental samples. For many elements, the technique is both extremely sensitive and interference-free. Nevertheless, the widespread use of the technique is hampered by a fundamental limitation: that is, a high-flux nuclear reaction must be available to provide a source of neutrons. Also, the analysis of large numbers of samples can be an expensive proposition, even when a reactor is routinely available. Because of these limitations, it is doubtful that neutron activation analysis will soon achieve a dominant role for routine elemental analysis of environmental samples such as biological specimens or ambient aerosols. Its sensitivity will continue to make it an extremely important technique in research, and for source characterization where the number of samples is small.

Recently, the National Academy of Sciences published a monograph entitled Neutron Activation Techniques for the Measurement of Trace Metals in Environmental Samples, by D.E. Robertson (Battelle Pacific Northwest Laboratories) and R. Carpenter (University of Washington, Seattle). This monograph is part of the NAS Nuclear Science Series.* Because this monograph summarizes so well the capabilities and limitations of neutron activation analysis, sections of it are reproduced here. This review will take the place of an original discussion, which otherwise would have had to be written.

Note that Robertson and Carpenter seem to have written the monograph from the point of view of measurements in and near the marine environment: emphasis is placed on marine-type aerosols, as well as marine waters, marine organisms, and marine sediments. Nevertheless, the discussion is more widely applicable.

Instead of a compilation of Instrument Notes, we shall merely list commercial firms which have come to our attention, and which provide instrumentation or analytical services in the field of neutron activation analysis. The 1973 Science Magazine "Guide to Scientific Instruments" (Vol. 182A, No. 4114A, 27 Nov. 1973) and the 1973 Analytical Chemistry "Laboratory Guide" list the following companies under the categories dealing with activation analysis:

Accelerators, Inc., Box 3293, Austin, TX 78764
Analog Technology Corp., 3410 E. Foothill Blvd., Pasadena, CA 91107
Canberra Industries, Inc., 45 Gracey Ave., Meriden, CT 06450
Charles Scientific, 295 Central Park West, New York, NY 10024
Harrison R. Cooper Associates, AMF Box 22014, Salt Lake City, UT 84122
EG&G/ORTEC, 500 Midland Rd., Oak Ridge, TN 37830
EDAX International, Inc., 103 Schelter Rd., Prairie View, IL 60069
INAX Instruments, Ltd., 306 Moodie Drive, P.O. Box 6044, Stn. J., Ottawa, Canada
Intelcom Industries, Ltd., Box 80817, San Diego, CA 92138
Kaman Sciences Corp., 1500 Garden of Gods Rd., Colorado Springs, CO 80907
Northern Scientific, Inc., 2551 W. Beltline Hwy., Middleton, WI 53562
Nuclear Data, Inc., Golf and Meacham Roads, Schaumburg, IL 60172
Nuclear Equipment Chemical Corp., 165 Marine St., Farmingdale, NY 11735
Nuclear Sources and Services, Inc., 5711 Etheridge, Houston, TX 77017
Tam-Sames, 21 Rue Jean Mace, Grenoble, France 38
Union Carbide Corp., 270 Park Ave., New York, NY 10017

In addition, a large number of companies besides those just tabulated can provide various components (e.g., semiconductor detectors, cryostats, pulse height analyzers).

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Neutron Activation Techniques for the Measurement of Trace Metals in Environmental Samples

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Foreword

The Subcommittee on Radiochemistry is one of a number of subcommittees working under the Committee on Nuclear Science within the National Academy of Sciences—National Research Council. Its members represent government, industrial, and university laboratories in the areas of nuclear chemistry and analytical chemistry.

The Subcommittee has concerned itself with those areas of nuclear science which involve the chemist, such as the collection and distribution of radiochemical procedures, the radiochemical purity of reagents, the place of radiochemistry in college and university programs, and radiochemistry in environmental science.

This series of monographs has grown out of the need for compilations of radiochemical information, procedures, and techniques. The Subcommittee has endeavored to present a series that will be of maximum use to the working scientist. Each monograph presents pertinent information required for radiochemical work with an individual element or with a specialized technique.

Experts in the particular radiochemical technique have written the monographs. The Atomic Energy Commission has sponsored the printing of the series.

The Subcommittee is confident these publications will be useful not only to radiochemists but also to research workers in other fields such as physics, biochemistry, or medicine who wish to use radiochemical techniques to solve specific problems.

Gregory R. Choppin, *Chairman*
Subcommittee on Radiochemistry

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I. INTRODUCTION

Anthropogenic wastes enter the environment via the atmosphere, and from direct discharges to aquatic and terrestrial surroundings. Once these pollutants have entered the environment they become entrained in complex biogeochemical and physical processes which serve to either disperse or reconcentrate the various contaminants. An essential feature of an effective environmental quality monitoring program is the capability for measuring these contaminants at near-background levels in the main matrices involved in pollution--fresh waters, sea water, atmospheric particulates, biological organisms and sediments and soils. Because the oceans are a major recipient of anthropogenic pollutants, the analyses of heavy metals in the marine environment will be emphasized in this treatise.

In monitoring the marine environment for metallic pollutants, few analytical methods offer the versatility and sensitivity achieved by neutron activation analysis (NAA). With the recent technological advances in developing high resolution solid state Ge(Li) detectors and their associated electronics, it is now possible to measure a wide spectrum of elemental constituents in virtually any environmental media by nondestructive, instrumental neutron activation analysis (INAA). Multielement analyses by this method is advantageous in two respects: (1) many of the potentially hazardous pollutant trace metals in various environmental matrices can be simultaneously measured and (2) many of the innocuous elements which greatly affect the biological availability and the biogeochemistry of the pollutant metals can likewise simultaneously be measured. When the concentrations of metallic pollutants are below the detection limits afforded by nondestructive INAA, either preconcentration or postirradiation separations of the elements of interest can be performed which, in most cases, increases the sensitivity for their measurement by orders of magnitude.

This monograph describes the technology and applications of NAA for the measurement of trace metal constituents in environmental samples, with emphasis placed on the marine environment. The contents are organized to indicate which trace elements can normally be measured by nondestructive INAA in the five matrices considered and, then when necessary, the chemistry required for preconcentrations and separations is provided. Emphasis has been placed on the measurement of the most potentially hazardous trace metals Hg, Cd, Cu, Ag, As, Sb, Cr, Se and Zn. Lead and tin are not included since NAA is not a sensitive method for these elements.

We stress the importance of analyzing only samples which have been collected and preserved to minimize contamination during these operations. Elaborate analyses of samples unrepresentative in time or space can also lead to erroneous conclusions. For both of these reasons we stress the need for good communication between the collector and the analyst. Precuations found effective in minimizing such undesirable artifacts of handling are discussed by Robertson (1972).

II. PRINCIPLES OF NEUTRON ACTIVATION ANALYSIS

Neutron activation analysis is a nuclear method of elemental analysis in which the elements in a sample to be analyzed are made radioactive by irradiation with neutrons and the induced radioactive species are then identified and measured. The amount of a given neutron activation product that is formed during neutron irradiation is directly proportional to the amount of its parent isotope. Measurement of the radionuclide provides a measure of the total concentration of the parent element.

The basic equation for activation is

$$W = \frac{AM}{\sigma f \phi (1-e^{-\lambda t}) \times 6.02 \times 10^{23}}$$

where W = weight of element irradiated, in grams
A = induced activity in disintegrations/sec at the end of irradiation
ϕ = flux of neutrons used in the irradiation, in neutrons/cm^2/sec
σ = the activation cross section for the nuclear reaction concerned, in cm^2
f = fractional abundance of the particular isotope of the element concerned
M = atomic weight of that element
λ = the decay constant of the induced radionuclide, in sec^{-1}
t = irradiation time, in seconds

From the above equation it is obvious that the detection sensitivity for a given element by this method can be improved by increasing the neutron flux and/or the irradiation time. The relative detection sensitivities for all of the elements in the periodic table are a function of their activation cross section for the nuclear reaction concerned, the decay constant of the induced radionuclide, the atomic weight of that element and the fractional abundance of the particular isotope of the element concerned. For most elements, NAA is an extremely sensitive method of analysis, as evidenced in Tables 1 through 7. A notable exception is lead, an important ocean pollutant which is best measured by isotope dilution-mass spectrometry, or possibly atomic absorption spectrometry.

The concentration of an element in a sample can be calculated from the above equation using a flux monitor and if the efficiency of the detector is known for the neutron activation product of interest. However, the easiest and most accurate method for quantifying the concentration of any element is to include with the irradiation of the sample a standard of known weight of the element being determined. Then the weight of the element being determined is obtained as follows:

$$\frac{\text{Weight of element in unknown}}{\text{Weight of element in standard}} = \frac{\text{Activity of element in unknown}}{\text{Activity of element in standard}}$$

This method obviates the need for careful neutron flux monitoring and counting instrument calibrations, since the only measurements that are required are the relative counting rates of the neutron activation products of the element of interest in the unknown and in the standard. This comparative method requires that the sample and standards be both irradiated and counted under the exact same conditions.

The neutron activation method of analysis does not distinguish between various physicochemical forms of an element in a particular sample, but provides a measure of its "total" concentration. However, if different physicochemical species of the same element are separated prior to the neutron irradiation, NAA can provide a measure of each specific form.

In practice, the fundamental steps in a typical NAA are:

1) Irradiate weighed quantities of the sample and standard in suitable containers for a sufficient time to give adequate radioactivity for the element to be determined.
2) After the irradiation, INAA is accomplished by simply counting the samples and standards on Ge(Li) and/or NaI(Tl) gamma-ray spectrometers at optimum times following the irradiation to directly measure elements producing short, intermediate and long-lived neutron activation products.
3) Compare the peak areas of samples and standards under identical counting conditions, making decay corrections, Compton corrections and background corrections when necessary.
4) If INAA does not provide the desired sensitivity, radiochemically separate the activation product(s) of interest from the interfering radionuclides and count the separates in the same geometries as the standards.

5) To insure that the gamma-ray being measured is due solely to the radionuclide of interest, check the half-life of the activity to be certain it is decaying at the proper rate. Further confirmation may be possible when the radionuclide emits more than one gamma-ray per disintegration, in which case both the energies and relative intensities can be used for verification.

For more detailed discussions of the basic theory, fundamentals and applications of NAA, the readers are referred to the following references: Anonymous (1971); Barbier (1969); DeVoe and LaFleur (1969); Guinn and Lukens (1965); Kruger (1971); Lenihan and Thompson (1969); Lutz et al. (1971) Rakevic (1970); Ryan (1973) and Smales (1967).

III. NEUTRON IRRADIATION FACILITIES AND PROCEDURES

The most generally applicable neutron source for trace level activation analysis is the high flux nuclear reactor. Most of these reactors normally operate at power levels in the range of 10 to 1000 kilowatts and produce thermal neutron fluxes of 10^{11} to 10^{13} n/cm^2/sec. Reactors used in such work are generally of the research type and are becoming increasingly available for use by the scientific community.

The neutron flux in such reactors varies spatially about the reactor core and inhomogeneities in the flux must be taken into account. Such inhomogeneities can be minimized by rotating the samples in the flux field in various types of specimen racks designed for that purpose. In a typical irradiation, up to 50 samples and standards can be irradiated in one rotator simultaneously. Although the horizontal neutron flux gradients in each rotator are minimized by revolving the samples, there exists a small vertical flux gradient which must be accounted for by placing a standard at each tier of samples if they are stacked vertically.

"Rabbit" irradiations are used for activating samples for periods of seconds to minutes, where the induced activity of interest is a short-lived isotope, one having a half-life in the range of seconds to minutes. Samples are activated and counted one at a time (usually purely instrumentally), with the reactor operating steadily and a standard sample of the element of interest similarly activated and counted at intervals.

IV. SAMPLE PREPARATION

A. Materials and Manipulations

A tremendous advantage of using INAA is that sample handling and manipulations are reduced to a minimum, thereby greatly reducing the probability of contaminating a sample. Contamination problems are particularly severe when dealing with natural waters. The problems of contamination in trace element analysis have been thoroughly dealt with in the literature (Robertson, 1968; 1972; Thiers, 1957 a, b).

Solid samples, such as sediments, biological tissue, air filters and sea and fresh water salts are normally weighed and heat sealed in cleaned polyethylene, polypropylene or high purity quartz vials ranging in size from 1 cc to 10 cc. Sample size can range from a few milligrams to tens of grams depending upon the sensitivity required and sample size available. Desiccation of sediments and biological tissue prior to encapsulation is accomplished by either freeze-drying or oven-drying at 105°C. Special precautions are necessary when drying samples for trace Hg analyses to avoid losses by volatilization. These precautions are discussed in the section dealing with mercury analysis by NAA.

Natural waters, especially seawater, must usually be evaporated to dryness if the samples are to be irradiated for more than several minutes, since gaseous radiolysis products (H_2, O_2 and other gases) are generated and produce high pressures which rupture the plastic irradiation vials. Problems due to pressure build-up are dependent upon the length of the irradiation, and almost any kind of sample can be irradiated for a few minutes. Desiccation can be accomplished by either freeze drying or slowly evaporating the water under an infrared heat lamp. Again, great care must be taken not to volatilize Hg and other volatile elements during these drying operations.

Water samples can be neutron irradiated directly, without evaporation, if the water is sealed in quartz vials. However, in the case of seawater, the radiolysis products build up dangerously high pressures which have even shattered sealed quartz vials and this method is not recommended for routine use. In addition, quartz contains much higher levels of impurities than polyethylene or polypropylene and is a potential source of contamination. Tanner et al. (1972), and Brune and Landstrom (1966) have described a method for neutron irradiating 30 to 80 ml samples of fresh water in a frozen state in polyethylene containers as a means of preserving the samples prior to and during the neutron irradiation.

It is important that samples in a given set be encapsulated in reproducible, identical geometries so that all samples will be neutron irradiated in a known orientation.

B. Elemental Standards

In multielement INAA, it is usually not practical to use separate individual elemental standards, and composite standards consisting of compatible mixtures of elements are preferred. Standard solutions containing 5 to 10 elements at optimum concentrations to provide good counting statistics and minimal interelement interferences can be conveniently prepared. Thus, only a few standard capsules need to be included in a large set of samples for neutron activation. It is important that standards for each element being measured be included in each irradiation. The use of flux monitors for intercomparison of irradiations made at different times and reactor fuel configurations should be discouraged, since some activation products are produced to a large degree by resonance capture of fast neutrons. The production of such activation products depends not only upon the neutron flux, but also upon the neutron energy spectra.

Elemental standards should be encapsulated and irradiated identically as the samples. Standards should be prepared in a matrix as close to the sample matrix as practically possible in order to minimize problems such as neutron self-shielding, irreproducible activation geometries and interfering nuclear reactions. Perlman and Asaro (1969) have discussed in some detail the necessity of carefully preparing standards in the same geometries and matrices which match, as closely as possible, that of the samples. For example, when neutron activating large quantities of sea salts, the elemental standards should be added to an equivalent amount of NaCl encapsuled in the same geometry as the sample. However, if sample sizes are kept very small, and the samples do not contain high concentrations of large cross section elements, exquisite matrix matching is not a critical requirement for the types of samples normally encountered in the marine environment.

The use of standard reference materials of known elemental composition as activation standards is a convenient method of simulating the sample matrix. Several reference materials are available for use as biological, environmental, and geological standards. The National Bureau of Standards (NBS) supplies orchard leaf, tuna meal and bovine liver as standard reference materials for analysis of biological material. Elemental concentrations in these materials are gradually being certified by NBS and they may become useful activation standards once their elemental concentrations are established. The Environmental Protection Agency (EPA) in cooperation with NBS has made up four environmental standards: fly ash, coal, oil and gasoline. Concentrations of a number of elements (especially those of prime environmental concern) will be established during 1973. The U.S. Geological Survey supplies a wide variety of geological standard reference materials which have reasonably well documented elemental concentrations (Flanagan, 1969; Fleischer, 1965). These rock samples are somewhat non-uniform for some elements, but represent the best available reference materials for analysis of marine sediments. Also, EPA has provided three freshwater sediments which many laboratories have analyzed for mercury. Two have mercury levels of ~ 45 and ~ 105 ppm Hg, respectively, which are much higher concentrations than normally found in natural sediments. The third has ~ 0.06 ppm and is at the lower end of most mercury values in sediments. These sediments are available in limited amounts from J. H. Finger, Environmental Protection Agency, Surveillance and Analyses Division, Athens, Georgia. Frequently, however, individual elemental standards must be prepared and included with the irradiations when the concentrations of those particular elements are not sufficiently high in the standard reference materials to be accurately measured.

To date, no standard reference natural water samples are available and analysts are required to prepare their own elemental standards. However, the EPA has made available six water reference samples which when diluted as prescribed will give different concentrations of As, Cd, Cr, Cu, Pb, Se and Zn in the ppb concentration range. These samples are available from J. A. Winter, Methods Performance Evaluation Activity, National Environmental Research Center, EPA, Cincinnati, Ohio, 45268.

C. Preconcentration and Postirradiation Separations

In most cases the only matrices that require preconcentration of some trace elements prior to neutron activation are fresh and sea waters, where the natural elemental concentrations are near or below the parts per billion range, thus requiring large volumes of sample to achieve the desired sensitivity. Atmospheric particulates are naturally preconcentrated from large volumes of air during their collection on various filter media. Generally, the trace metal levels in marine organisms, sediments and atmospheric particulates are sufficiently high so that convenient sized samples can be neutron activated and postirradiation radiochemical separations be performed.

Postirradiation separations are usually the most desirable, because once the radioactive species are produced, any amounts or types of stable reagents and labware can be used in the chemical manipulations without contaminating the samples with the elements being measured. However, in the case of sea salts, if trace elements with short-lived (< 1 to 2 days) neutron activation

products are to be measured, the trace elements must be separated from the NaCl matrix before neutron irradiation, since high radiation doses result from the large concentrations of ^{24}Na and ^{38}Cl which are produced when sea salts are neutron activated.

Preconcentration schemes for natural waters can be very simple, involving perhaps only the removal of much of the major activity component, such as ^{24}Na. Alternatively, the separations can be made groupwise, and both such procedures are usually followed by gamma-ray spectrometry to obtain final specific measurement of each individual neutron activation product. Occasionally, and especially where the highest possible sensitivity is required, very thorough preconcentration or postirradiation separations are necessary. In the following sections chemical separation schemes are given for those elements of interest which cannot be measured in the various matrices by purely INAA.

V. GAMMA-RAY SPECTROMETRY

Since all of the elements of interest in this work, except Pb and Sn, form neutron activation products with easily measurable gamma-rays, this section will be concerned only with gamma-ray spectrometry involving solid state Ge(Li) diode detectors and NaI(Tl) scintillation crystals.

A. Ge(Li) Diode Spectrometry

Lithium drifted germanium detectors have revolutionized INAA because of their excellent energy resolving capability (about 2 to 3 keV FWHM above about 200 keV). Even better resolution can be attained at energies below about 200 keV utilizing low energy photon detectors (LEP detectors). These detectors will allow increasing use of low energy gamma-rays and X-rays for INAA. Heretofore, single NaI(Tl) crystals were capable of resolving only a few of the major constituents in complex mixtures of radionuclides. Ge(Li) detectors, however, can resolve the gamma rays of nearly all neutron activation products formed in marine environmental matrices, if their concentrations are sufficiently high to be detected. Gamma-ray energies can be determined to within ± 0.3 keV, and the energies of nearly all neutron activation products are now known to ± 0.1 keV. A good example of this improved resolution is shown in Figure 7, which compares the gamma-ray spectra of neutron activated sea salts counted on both a NaI(Tl) crystal and a Ge(Li) diode detector. The main disadvantage of Ge(Li) detectors is their relatively low efficiency, compared to NaI(Tl) crystals. However, for most neutron activated samples the low efficiency of the Ge(Li) detectors is not a serious problem, since sufficiently high concentrations of the neutron activation products of the elements of interest can normally be produced in high flux nuclear reactors.

The basic principles and applications of Ge(Li) diode detectors have been adequately described in the literature (Bertolini and Coche, 1968; Brown et al, 1969; Camp, 1967; Cooper, 1973; Dearnaley and Northrop, 1966; Heath, R. L., 1969; Hollander, 1966; Keil and Bernt, 1972; Lutz et al, 1971). Briefly, the hardware required for a basic Ge(Li) gamma-ray spectrometer is the Ge(Li) detector, a preamplifier, an amplifier, and a 2000 or 4000 channel pulse height analyzer.

While Ge(Li) detector systems of greater versatility and sophistication have been constructed (for example, Cooper and Perkins, 1972) ordinary Ge(Li) detector systems are adequate for measuring a large group of neutron activation products in environmental samples.

In practice, the neutron activated samples and standards are transferred from the irradiation containers into standard counting geometries, which may consist of polyethylene vials of various sizes or some other suitable containers. Care must be taken to assure that the samples and the standards are encapsulated in identical counting geometries. Relatively small differences in orientation of the samples and standards within the containers can lead to serious errors if the containers are counted on or close to the Ge(Li) detector. This is especially important for such unusually shaped samples as filters and resins. One must not be seduced into placing the samples on the detector to increase counting efficiency without experimentally evaluating the geometry factors. The samples and standards are then positioned on or near the Ge(Li) detector in a fixed geometry and counted for a sufficient length of time to achieve the necessary counting statistics. Differences in geometries in a set of samples can be minimized by counting the samples several cm away from the Ge(Li) detector if sufficient activity is present.

B. NaI(Tl) Spectrometry

NaI(Tl) detector systems are most useful when sensitivity is the main concern, since NaI(Tl) detectors are approximately 10 to 100 times more efficient than Ge(Li) diode detectors. NaI(Tl) crystals of various geometries are commercially available but the most commonly employed are well crystals or solid, cylindrical crystals of various sizes normally ranging from about 3 to 13 inches in diameter and about 3 to 9 inches thick. The background and Compton response of these crystals can be substantially lowered by anticoincidence shielding with large plastic phosphors or annular NaI(Tl) crystals (Perkins and Robertson, 1965; Wogman et al, 1967, for examples). Two large anticoincidence-shielded NaI(Tl) detectors can be designed to count as dual coincidence gamma-ray spectrometers, thereby greatly increasing the sensitivity and selectivity of NaI(Tl) gamma-ray spectrometry (Perkins and Robertson, 1965).

These large crystal NaI(Tl) systems are particularly applicable for measuring traces of neutron activation products which have been radiochemically separated from an interfering matrix. Their high efficiencies permit very low levels of radioactivity to be measured in relatively short counting intervals.

C. Data Handling

Interpretation of gamma-ray spectra obtained from NaI(Tl) and Ge(Li) detectors typically involves location of peaks in the spectra, determination of peak energies, measurement of peak areas and calculation of concentrations of the elements from which the gamma-ray emitters were formed. In NaI(Tl) spectrometry, if the radionuclide mixture is quite simple, the peak areas can be obtained by manual subtraction of background and Compton contributions. However, if the radionuclide mixture contains more than 3 or 4 gamma emitting radionuclides, the spectrum stripping is most conveniently and accurately accomplished by using a computer program designed for that purpose. Because peak areas in Ge(Li) diode spectra are normally well resolved, determination of peak intensities by manual subtraction of the background and Compton contribution can be readily accomplished in even very complex mixtures of radionuclides. Normally, an equal number of channels on each side of the peak area are selected to represent the contribution due to background and Compton interferences and this contribution is manually subtracted from the peak area. However, if many routine analyses are required, the manual method can become tedious and time consuming and the most rapid and economical way to process the data is with a computer.

The development and application of computer programs for the analysis of gamma-ray spectra is, by no means, an elementary task. For computer analysis to be workable, spectrometer systems must be very electronically stable, precisely adjusted before counting and the spectra must be converted to a computer compatible form. Incorrect input of data confuses a computer, resulting in termination of the analysis or computation of wrong answers. Once these problems have been overcome, a computer analysis of the gamma-ray spectra is capable of rapidly converting the spectra directly into concentrations of individual constituents. However, unless one is tooling up for the analysis of a large number of routine samples, it is often more trouble than it is worth to develop a computer program designed to quantify INAA. It is a good practice to occasionally check computer programs by hand calculations to ensure that they are operating as designed.

For more detailed discussions of the use of computers for data reduction the readers are referred to the following material: DeVoe and LaFleur, 1969; Salmon and Creevy, 1970; O'Kelley, 1962.

VI. ELEMENTAL ANALYSES

A. Fresh Waters

1. Instrumental Neutron Activation Analysis

Nearly all of the potential pollutant elements of interest can be measured in fresh waters (atmospheric precipitation, rivers, lakes, tap water, etc) by INAA utilizing a very simple radiochemical group separation to remove interfering neutron activation products. Figure 1 illustrates the relative abundances of the major and some of the minor radionuclides formed during neutron activation of Columbia River water and their change in concentration with time. It is obvious that the high activity due to ^{24}Na (Columbia River water contains about 2 mg Na/ℓ) will mask the gamma-ray spectra of all of the trace neutron activation products of the elements of interest, except ^{38}Cl, ^{42}K, ^{56}Mn and possibly ^{87m}Sr. Therefore, to measure the short-lived neutron activation products of As, Hg, Cu, Zn, Ba and La, as well as several other elements of geochemical interest, it is necessary to remove the interfering ^{24}Na.

Tanner et al. (1972) have described a simple two-step separation scheme which eventually permits the semi-instrumental measurement of about 19 trace elements (see Figure 2). The method simply consists of passing a neutron activated water sample, containing carriers of 0.1 mg each of Na, K, Rb and Cs, through a column of Dowex 1x2 anion exchange resin which has been converted to OH^-, $S^=$ and $CO_3^=$ forms by contacting with $1\underline{M}$ solutions of NaOH, Na_2S and Na_2CO_3, respectively. All trace activation products, except the alkali metals and the alkaline earths, are retained on the resins by precipitation-ion exchange mechanisms. The combined resin is then rinsed with distilled water, transferred into a plastic counting container and counted directly on a Ge(Li) detector. The column effluent, containing the radionuclides ^{24}Na, ^{42}K, ^{86}Rb, ^{134}Cs and traces of neutron activation products of the alkaline earths Ca, Ba and Sr, is treated with an excess of 4% sodium tetraphenylboron to

FIGURE 1

RELATIVE CONCENTRATIONS OF INDUCED RADIONUCLIDES IN COLUMBIA RIVER WATER FOLLOWING AN INTEGRAL NEUTRON IRRADIATION OF 2 × 10^{16} n/cm^2, EMPHASIZING THE PROBLEM OF MEASURING SHORT-LIVED ACTIVATION PRODUCTS BY INAA IN THE PRESENCE OF HIGH CONCENTRATIONS OF SODIUM-24

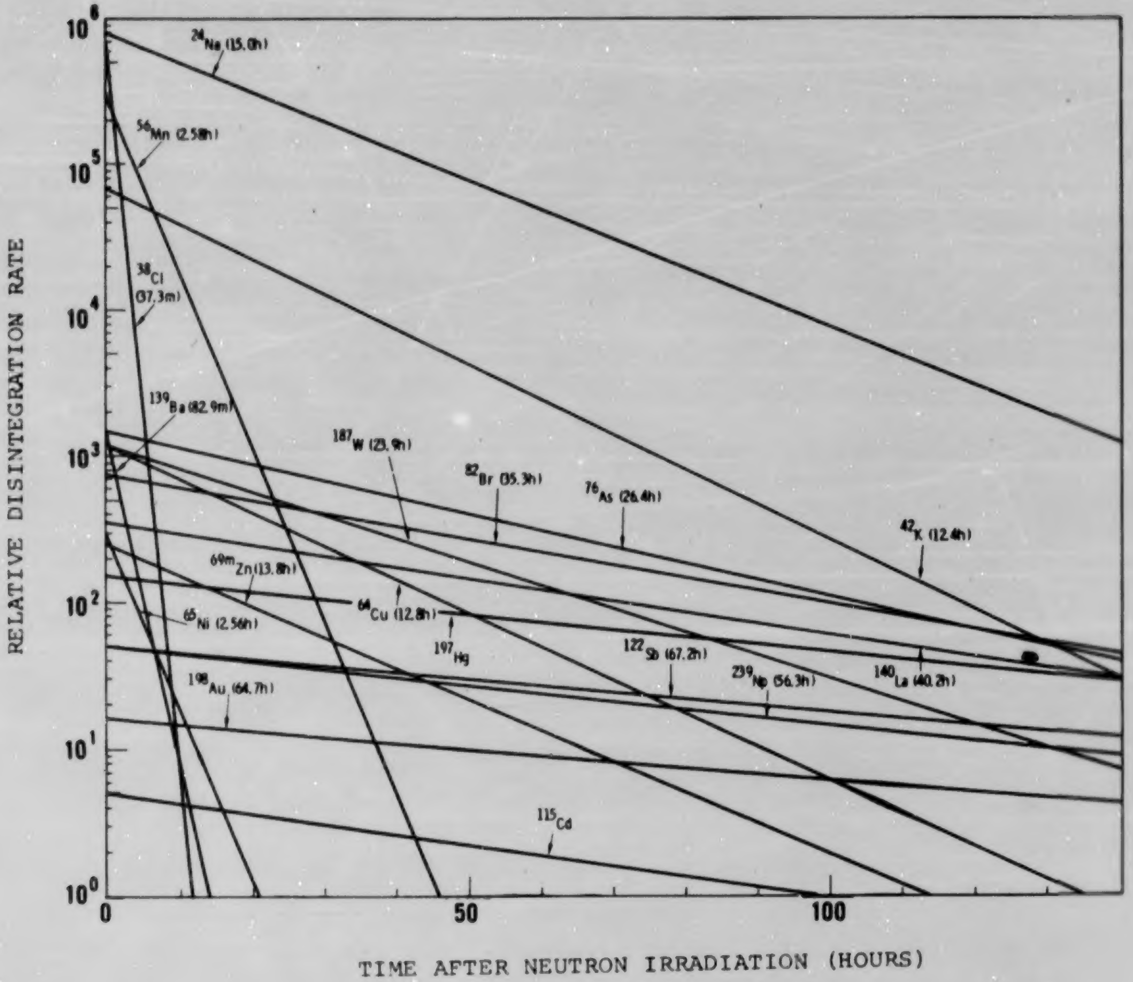
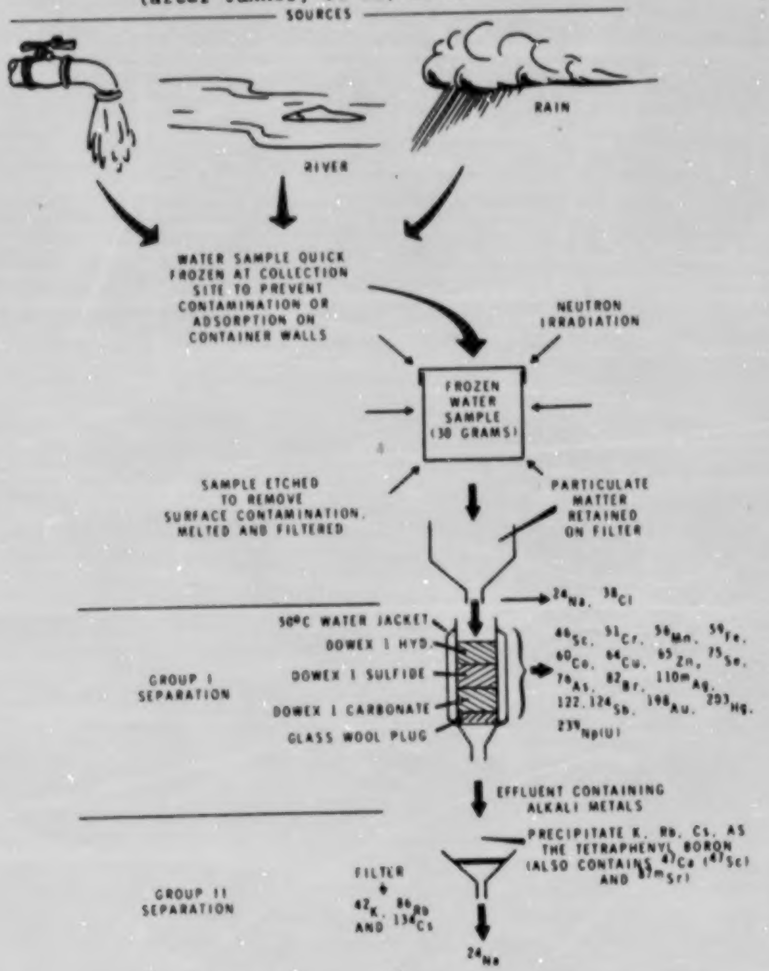


FIGURE 2

MULTIELEMENT ANALYSIS OF TRACE CONSTITUTENTS IN NATURAL WATER BY NEUTRON ACTIVATION, TWO-GROUP CHEMICAL SEPARATIONS AND GAMMA-RAY ANALYSIS
(after Tanner, et al, 1972)

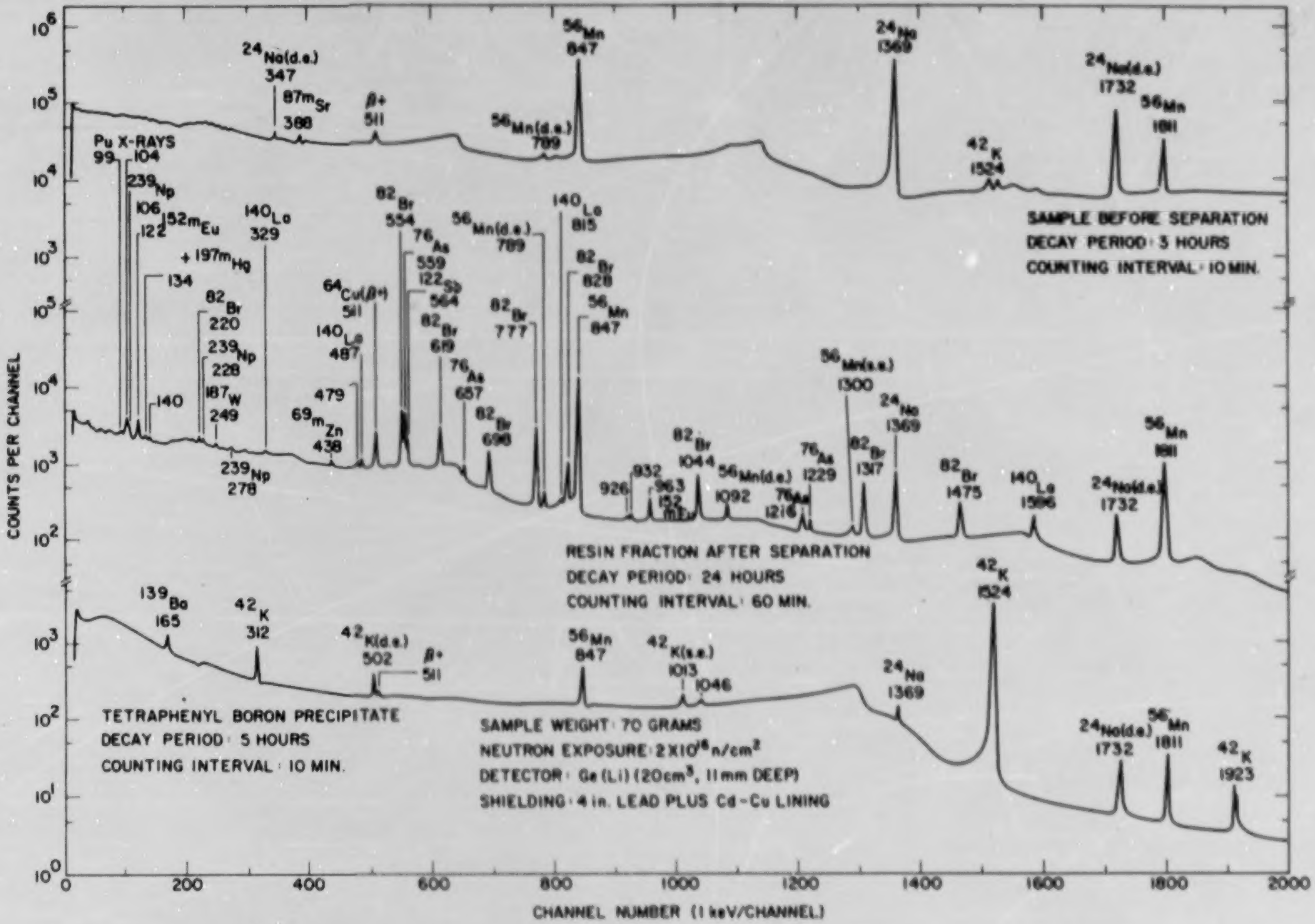

SOURCES
RIVER
RAIN
WATER SAMPLE QUICK FROZEN AT COLLECTION SITE TO PREVENT CONTAMINATION OR ADSORPTION ON CONTAINER WALLS
NEUTRON IRRADIATION
FROZEN WATER SAMPLE (30 GRAMS)
SAMPLE ETCHED TO REMOVE SURFACE CONTAMINATION, MELTED AND FILTERED
PARTICULATE MATTER RETAINED ON FILTER
^{24}Na, ^{38}Cl
50°C WATER JACKET
DOWEX 1 HYD.
DOWEX 1 SULFIDE
DOWEX 1 CARBONATE
GLASS WOOL PLUG
GROUP I SEPARATION
^{46}Sc, ^{51}Cr, ^{54}Mn, ^{59}Fe, ^{60}Co, ^{64}Cu, ^{65}Zn, ^{75}Se, ^{76}As, ^{82}Br, ^{110m}Ag, ^{122,124}Sb, ^{198}Au, ^{203}Hg, ^{239}Np(U)
EFFLUENT CONTAINING ALKALI METALS
PRECIPITATE K, Rb, Cs, AS THE TETRAPHENYL BORON (ALSO CONTAINS ^{47}Ca (^{47}Sc) AND ^{87m}Sr)
FILTER
^{42}K, ^{86}Rb AND ^{134}Cs
GROUP II SEPARATION
^{24}Na

precipitate Cs, K and Rb. The precipitate is washed, filtered and counted directly on a Ge(Li) detector. Standard solutions of the elements of interest are sealed in quartz vials, irradiated, transferred to plastic counting containers and counted in the same geometries as the samples to quantify the measurements by the comparator method. Figure 3 illustrates the gamma-ray spectra of the short-lived radionuclides measured in neutron activated Columbia River water before and after the separation scheme. Figure 4 illustrates the gamma-ray spectra of the long-lived neutron activation products contained on the resins and tetraphenylboron precipitate by counting 23 and 24 days after the irradiation. Eleven additional neutron activation products can be detected from these counts.

In Table 1 the elements which can normally be measured in fresh waters by this semi-INAA technique are indicated, together with the detection limits of many of the elements of interest. Without any separations at all it would still be possible to measure Ag, Br, Cl,Co, Cr, Cs, Fe, Mn, Na, Rb, Sb, Sc, Se, U, Zn, Ag and occasionally Hg, simply by counting the neutron activated river water samples at several optimum times following the irradiation (approximately 4 hours, 3 days and 20 days). The radiochemical separations permit the measurement of As, Cu, La and K.

Table 1 also lists the approximate limits of detection for 20 elements in river water utilizing the method of Tanner et al. (1972), and compares these limits with maximum allowable concentrations of some of the more toxic heavy metals in drinking water, as established by the U. S. Public Health Service. As indicated in Table 1, this semi-INAA technique can be used to detect most heavy metal pollutants in fresh waters at concentrations well below maximum permissible limits. Of the most toxic heavy metals, only Cd, Pb, Sn and occasionally Hg cannot be measured by this method.

FIGURE 3 **GAMMA-RAY SPECTRUM OF NEUTRON ACTIVATED RIVER WATER**
(after Tanner, et al, 1972)



SAMPLE BEFORE SEPARATION
DECAY PERIOD: 3 HOURS
COUNTING INTERVAL: 10 MIN.

RESIN FRACTION AFTER SEPARATION
DECAY PERIOD: 24 HOURS
COUNTING INTERVAL: 60 MIN.

TETRAPHENYL BORON PRECIPITATE
DECAY PERIOD: 5 HOURS
COUNTING INTERVAL: 10 MIN.

SAMPLE WEIGHT: 70 GRAMS
NEUTRON EXPOSURE: 2×10^{16} n/cm^2
DETECTOR: Ge(Li) (20cm^3, 11mm DEEP)
SHIELDING: 4 in. LEAD PLUS Cd-Cu LINING

FIGURE 4 **GAMMA-RAY SPECTRUM OF NEUTRON ACTIVATED RIVER WATER**
(after Tanner, et al, 1972)

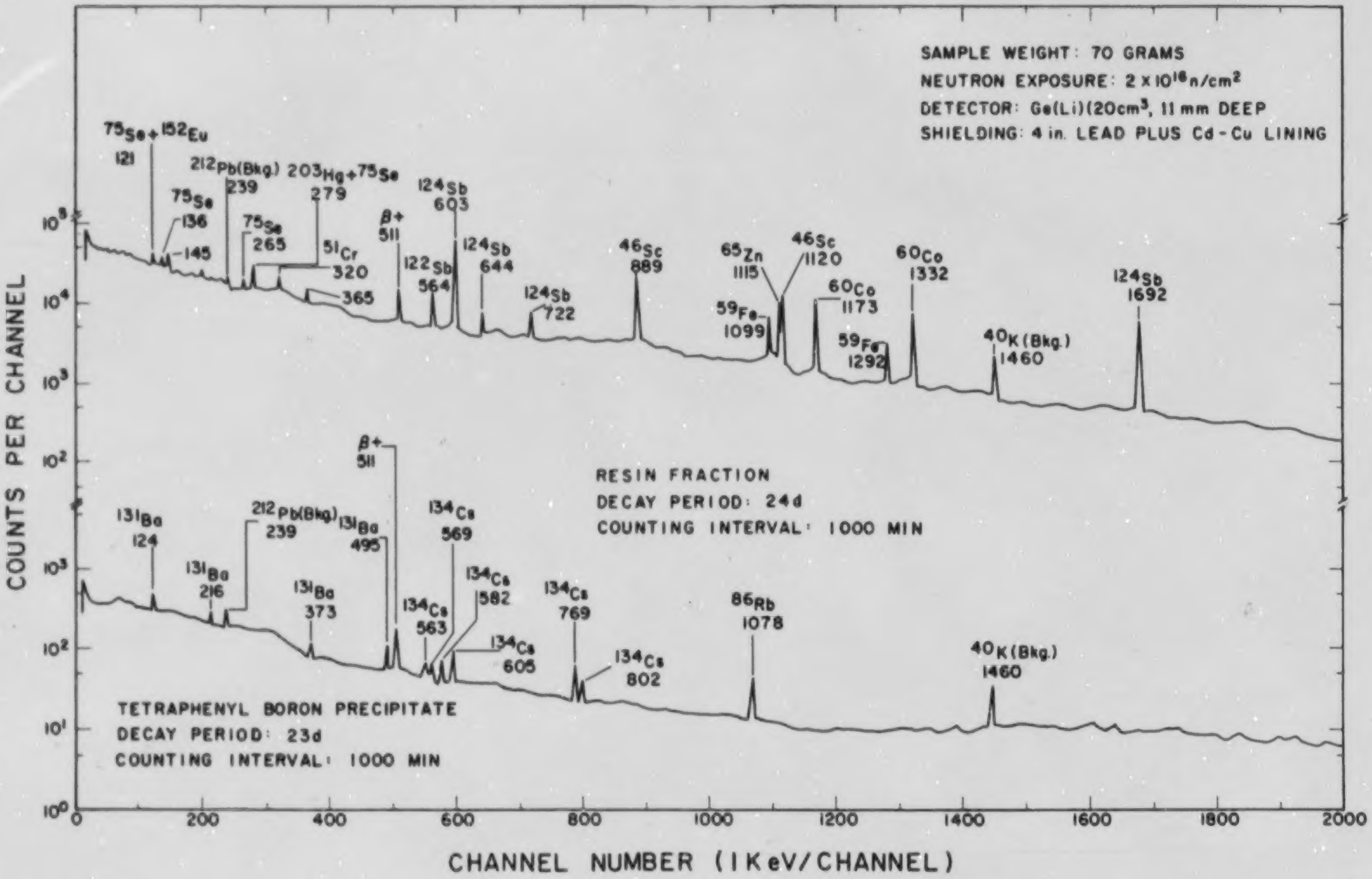


TABLE 1

APPROXIMATE LIMITS OF DETECTION OF VARIOUS TRACE METALS IN RIVER WATER BY NEUTRON ACTIVATION AND GROUP SEPARATIONS

Element	Approx. Estimate of Conc. in River Waters (μg/l) (a)	Detection Limits by NAA After Group Separation (μg/l) (b)	Allowable Limits (μg/l) (c)
Ag*	0.3	0.01	50
As	2	0.1	50
Ba	10	5	1000
Br*	20	0.01	
Cd	--	50	10
Cl*	7800	100	
Co*	0.2	0.01	
Cr*	1	0.1	50 (Cr^{+6})
Cs*	0.02	0.01	
Cu	7	0.1	1000
Fe*	--	10	300
Hg	0.07	0.1	(10)
K*	2300	10	
Mn*	7	0.01	50
Na*	6300	10	
Rb*	1	0.1	
Sb*	0.3	0.01	
Sc*	0.004	0.001	
Se*	0.2	0.1	10
Zn*	20	1	5000

* Elements normally detected and measured by INAA

(a) after Turekian (1969)

(b) after method of Tanner et al. (1972)

Thirty to eighty ml water samples; integrated thermal neutron exposure 2×10^{16} n/cm^2; count for 10 min., 60 min., and 1000 min. after decay times of 3 hrs, 24 hrs and 23 days, respectively; 20 cc Ge(Li) detector.

(c) U. S. Public Health Service (1962).

Edgington and Lucas (1971) and Girardi and Sabbioni (1968) have developed a method of removing ^{24}Na, the major interference in NAA of environmental samples, based on selective retention of the ^{24}Na on hydrated antimony pentoxide (HAP). All neutron activation products, except ^{24}Na, ^{182}Ta and ^{233}Pa, reportedly pass through the HAP column and are measured by Ge(Li) gamma-ray spectrometry. The method of Edgington and Lucas (1971) provides a breakdown into further group separations by selective elution of the effluent from the HAP separation from Dowex 1x8 anion exchange resin.

Neutron activation analysis is not a sensitive method for Pb and Sn, but Cd can be measured by preconcentration from 500-1000 ml of fresh water. Since Hg and Ag are normally present in uncontaminated fresh waters at concentrations near or below their detection limits for INAA, preconcentration or post irradiation separations are described below for these elements, as well as for Cd.

Suspended Particulate Matter

Particulate matter suspended in natural waters carry significant percentages of the total amounts of several elements in the waters. To determine the partitioning of the elements between the two phases, it is desirable to isolate the suspended particulate material, by either centrifugation or membrane filtration. The preferred method is by membrane filtration, and the usual filter pore size used is about 0.3 to 0.5μ. Both Millipore ® and Nuclepore ® filters have commonly been used for this purpose, and both filters contain roughly comparable traces of most impurities. It is recommended that as large a water sample as practically possible be filtered to obtain enough suspended matter for elemental analysis and to reduce the probability of contamination of the filtered water during the filtering process. The first several hundred ml of filtrate should be discarded because of contamination which may be leached from the filters.

Several types of all-plastic filtering devices are commercially available (Millipore Corporation; General Electric Co., for examples) which are suitable for filtering natural waters. The usual procedure for INAA of suspended particulates is to collect the material on tared filters (Millipore ®, Nuclepore ®, etc.), dessicate to constant weight and reweigh the filters to obtain a gravimetric analysis. The weighed filters are then encapsuled in plastic irradiation vials and neutron activated, together with appropriate standards of the elements of interest. After the irradiation, the samples are then counted on a Ge(Li) detector at optimum decay times to measure up to 24 trace elements. Since the suspended particulate matter in natural waters is usually a combination of both geological and biological material, the discussion of which elements can be measured and the detection sensitivities which can be achieved will be covered in the following sections concerned with analyses of biological and geological material.

Several problems may arise during this procedure. The filters themselves may lose weight when large volumes of water are filtered through them. The concentrations in the filters of many elements of interest vary considerably from filter to filter and from batch to batch, creating a large uncertainty in the blank than one would like. The filters may become friable due to irradiation damage under long irradiations at high neutron fluxes, leading to problems in subsequent manipulations with the filters. Weighing of membrane filters on an analytical balance may present some problems due to the electrostatic charge which accumulates on the filters. This can be overcome by inserting a special α-emitting Po source (Watson Brothers, Northern California Division, Scientific Instruments, San Mateo, California) inside the balance case. The ionization of the air produced by the alpha particles neutralizes the electrostatic charge on the membrane filter. Nuclepore ® filters appear to offer the most desirable taring characteristics because they absorb less moisture than other types of membrane filters.

2. Analysis of Elements Requiring Preconcentration or Postirradiation Separations

The trace metals of pollution concern which frequently need to achieve the necessary sensitivity for NAA are Hg, Cd, Ag, As and Se. Procedures are given below which accomplish these separations.

Under certain conditions, mercury losses by diffusion through polyethylene irradiation containers during neutron activation of fresh waters have been reported (Bate, 1971). Individual investigators should evaluate their particular methods of encapsulating and irradiating natural waters to insure that such losses are not significant. One method of minimizing such losses is to irradiate the water sample in a frozen state, as indicated in the following procedure.

Mercury Procedure I

Landstrom and Wenner (1965) have reported a simple procedure for the isolation of ^{203}Hg from neutron activated natural water samples. A 30 ml water sample, neutron irradiated in a frozen state for 12 hours at a flux of about 2×10^{12} n/cm^2/sec, is transferred to a distillation flask and acidified with H_2SO_4. Hydrogen peroxide and HBr are added and the Hg is distilled as the bromide. The distillate is made 3.5 $\underline{M}$ in H_2SO_4 and 0.1 $\underline{M}$ HCl, H_2O_2 is added, Br is driven off and the solution is passed through a small column of Dowex 2x10 anion exchange resin in the sulfate form. The column, containing the sorbed Hg, is rinsed with 0.1 $\underline{N}$ HCl to elute Sb, As, and Se and the anion resin is then counted to determine $^{197-203}$Hg activity. Mercury standards, irradiated with the samples, are counted in the same geometry to quantify the measurements. Recovery is reported to be 96%.

Mercury Procedure II

Ljunggren et al. (1971), have reported a method for separating radiomercury from neutron activated fresh waters. Water samples 0.2 to 10 ml in volume are sealed in cleaned quartz vials and irradiated for 2 to 3 days in a thermal neutron flux of about 3-4 x 10^{12} n/cm^2/sec. After a short cooling period, the samples and 20 mg of Hg carrier are digested in the Bethge apparatus with 15 ml of 10:1 mixture of concentrated nitric acid and sulfuric acid. To the digested solution is added a mixture of 5 ml of 70% perchloric acid and 0.5 gm of glycine in 5 ml of water. The Hg is distilled from the solution until the temperature reaches 250°C. The distillate (containing the Hg) is diluted to about 300 ml with distilled water and Hg is electrodeposited on a tared thin gold foil. A platinum foil (2 x 3 cm) is used as an anode and a thin gold foil (1 x 3 cm) as the cathode, and these electrodes are immersed in the electrolyte about 6 cm apart. About 95% of the Hg is electrodeposited after 15 hours of electrolysis at a voltage of 4 to 6 volts and a current of 0.3 to 0.5 ampere. When the electrolysis is completed, the electrolyte is neutralized with NH_4OH, using phenol red as an indicator. Before the current is interrupted, the gold foil is removed from the solution, and rinsed with distilled water and alcohol. The electrical contacts are then removed and the gold foil is dried and reweighed to obtain the chemical yield. The foil is sealed in a plastic bag and the $^{197-203}$Hg activity is measured by gamma-ray spectrometry. The use of a sample of 10 ml places the detection limit at 0.01 ng/ml.

Mercury Procedure III

Brune and Jirlow (1967) have developed a method for separating radiomercury from neutron activated fresh water samples based on the isotopic exchange technique reported by Kim and Silverman (1965). Water samples are neutron irradiated in polyethylene containers in a frozen state for 3 to 13 hours at a flux of about 2 x 10^{12} n/cm^2/sec. After the irradiation, the water samples are transferred to a distilling flask equipped with a reflux condenser. A 3:1 mixture of nitric and sulfuric acid is added and the sample refluxed for about 20-40 minutes. The solution is cooled and then diluted with an equal volume of water, and the pH is adjusted to 1 to 2 by addition of NH_4OH. The solution is transferred to an appropriate sized bottle and 0.5 gm of NH_4Br is added, followed by 0.2 ml of elemental inactive Hg. The solution is vigorously stirred for 40 minutes to allow the radiomercury to exchange with the inactive Hg. The Hg is then separated on a sintered glass filter disk, washed with water and acetone, and then dissolved in 5 ml of concentrated nitric acid. The nitric acid is transferred to an appropriate container and $^{197-203}$Hg is measured by gamma-ray spectrometry.

Mercury Procedure IV

Thatcher and Johnson (1971) have developed a precipitation method for measuring Hg in fresh waters by NAA. Water samples are placed in 20 ml quartz vials which are immediately sealed. The vial is neutron irradiated for 4 hours in a flux of 5 x 10^{12} n/cm^2/sec. One day after the irradiation the vial is opened, carrier Hg in nitric acid is added and the sample is allowed to stand one hour to desorb any radioactive Hg from the quartz. The sample is transferred to a polyethylene centrifuge tube and ammonium persulfate is added to oxidize organo-mercurials. Sodium bisulfite is added to reduce excess persulfate and todilute ^{24}Na and ^{35}S activities. Stannous chloride is next added to precipitate metallic mercury. The precipitate is centrifuged and counted for ^{197}Hg. Sensitivity is 0.05 μg/l but could be improved by simply activating the samples for a longer period of time.

The above four methods are capable of measuring only "total" mercury (inorganic plus organic forms), since the post-irradiation digestion procedures should destroy any organically bound Hg. Although these four procedures have been developed especially for neutron activation analysis of Hg in fresh waters, there are numerous postirradiation radiochemical separation schemes developed for other matrices which can be slightly modified to meet the needs of fresh water analyses. These procedures are contained in an excellent monogram by Roesmer (1970).

If Hg concentrations in fresh waters are too low to measure in 1 to 30 ml volumes as described in the above procedures, preconcentration from large volumes (0.2 to 2 liters) of water is necessary. Lai and Weiss (1962) have described a very simple preconcentration procedure, which has subsequently been used at Battelle-Northwest Laboratory (Robertson, unpublished work, 1972) for preconcentration of Hg from seawater and should be applicable to fresh waters. A water sample (0.2 to 2 liters) is adjusted to a pH of 3.5 to 8, warmed to about 60°C and 20 ml of a 1% solution of thionalid in acetone is added. The water samples are then chilled in a refrigerator and the thionalid crystals (containing quantitatively cocrystallized Hg) are collected on membrane filters, washed with high purity water, and encapsulated in polyethylene vials for neutron activation analysis. ^{203}Hg can be directly measured in the neutron activated thionalid by Ge(Li) gamma-ray spectrometry several weeks after the irradiation.

Weiss and Crozier (1972) have described a method of preconcentrating Hg from seawater, which should be equally applicable to fresh waters. Mercury is separated from 500 ml of water by adding 1 mg of Cu carrier and coprecipitating the Hg with the Cu as sulfides by bubbling H_2S gas into the water for 30 second. The CuS precipitate is collected by membrane filtration, washed with high purity water and encapsulated in a polyethylene vial for neutron activation. After the irradiation the $^{197-203}$Hg is radiochemically separated and measured by gamma-ray spectrometry.

Minczewski (1967), Mizuike (1965) and Joyner (1967) have described a number of group preconcentration procedures which should be adaptable for separating Hg from large volumes of water.

Cadmium Procedures

Landstrom and Wenner (1965) have outlined a postirradiation radiochemical separation scheme for the measurement of Cd by neutron activation analysis, based on its anion exchange properties. However, the method is not generally applicable, because it lacks the sensitivity to measure environmental levels of Cd in only 10 to 30 ml of fresh waters. Therefore, it is necessary to preconcentrate the Cd from large volumes (0.2 to 2 liters) of water prior to the neutron activation step. Riley and Taylor (1968) and Goya and Lai (1967) have described a preconcentration method for Cd in seawater, based on adsorption onto Chelex-100 chelating resin, and this method should be adaptable to fresh waters. Other preconcentration schemes, as outlined by Minczewski (1967) and Mizuike (1965) should be rather easily adaptable for preconcentrating Cd from large volumes of fresh waters.

After the preconcentrates have been neutron activated, appropriate radiochemical separations as outlined by Devoe (1960) may be used to further isolate the radiocadmium.

Silver Procedures

Kharkar, et al. (1968) have measured Ag in river waters by NAA. Their procedure is to irradiate freeze-dried river salts, having added 25 mg of spec-pure Na_2CO_3 per 100 ml of river water to provide enough salts with which to conveniently work. Several weeks after the irradiation the salts are dissolved in 20 ml of 1 N HCl and silver carrier is added. Silver chloride is filtered off, rinsed with 0.1 N HCl, dissolved in a small volume of HNO_3 and then converted to an NH_4OH solution. The solution is scavenged with $Fe(OH)_3$ to remove interferences and the Ag is then precipitated with H_2S. The precipitate is dissolved in concentrated HNO_3, diluted with water and the Ag is reprecipitated in dilute HCl. The AgCl precipitate is washed, dried and counted for ^{110m}Ag.

The same thionalid preconcentration procedure (Lai and Weiss, 1962) described earlier for Hg can be used to isolate Ag from large volumes of fresh waters, to achieve the desired sensitivity. Silver can then be directly measured by counting the neutron activated thionalid crystals (containing quantitatively cocrystallized Ag) on a Ge(Li) diode detector or dual coincidence gamma-ray spectrometer. If further radiochemical purity is required, the method of Kharkar et al. (1968), can be used.

Arsenic Procedures

Arsenic can usually be measured in river or lake waters by the semi-INAA method of Tanner et al. (1972). However, in some natural waters, particularly precipitation, the As must be preconcentrated from large volumes of water. The As procedures described in the following section for seawater analyses are completely applicable for the determination of As in fresh waters.

Selenium Procedure I

For some natural waters the Se must be preconcentrated to achieve the necessary sensitivity. Kharkar et al. (1968) have developed a separation scheme for measuring Se in fresh waters. One hundred ml of freeze-dried river salts (containing 25 mg of spec-pure Na_2CO_3/100 ml of river water as a salt carrier) is neutron activated. Several weeks after the irradiation the sample is dissolved in 1 N HCl, carriers are added, AgCl is filtered off and the solution is made 6 N in HCl and H_2S added to precipitate Mo and Se sulfides. The Mo sulfides are dissolved away in dilute HNO_3 and the Se sulfide is purified by dissolving in concentrated HNO_3, precipitating Se with SO_2, distilling off Se as the bromide and finally reducing Se as the metal with $NaHSO_3$. The Se metal is filtered, washed, dried and counted to measure ^{75}Se activity.

Selenium Procedure II

Weiss, et al. (1971) have measured Se in melted samples of the Greenland ice sheet by NAA. One to 4 liter samples are acidified with HNO_3 and evaporated to 1 ml and neutron activated. After the irradiation the Se is radiochemically separated by repeated precipitations of the Se metal carrier. The final Se precipitate is filtered and beta-counted in a gas-flow proportional counter periodically to measure ^{81}Se and check its half-life. Yield is checked by counting carrier-free ^{75}Se added at the start of the procedure. Selenium concentrations as low as 5 ng/kg were measured.

Chromium Procedures

Chromium is frequently below the detection limit of INAA and must be preconcentrated from large volumes of fresh waters. The methods given for Cr measurements in the following section on seawater analysis are directly applicable for fresh waters.

Suspended Particulate Matter

The pollutant elements of concern contained on separated suspended particulate matter can be analyzed by post-irradiation radiochemical separations once the material has been properly digested. Refluxing in $HNO_3-H_2SO_4$ is normally a sufficient digestion procedure if siliceous materials are not present. If large amounts of silica are present, HF must be added to the acid digest to volatilize the silica. Care must be exercised to insure that volatile elements such as Hg are not lost during the digestion procedure.

B. Seawater

1. Instrumental Analysis

Because of the tremendous amounts of ^{24}Na (15.4 hrs) which are produced during neutron irradiation of seawater, INAA of seawater is applicable only for those elements in seawater which have relatively long half-life activation products. From Figure 5, it is obvious that none of the short-lived neutron activation products of interest could possibly be measured instrumentally, since the ^{24}Na, ^{38}Cl, ^{42}K and ^{82}Br are orders of magnitude more abundant, and completely mask the gamma-ray contributions of the activation products of interest. For the INAA of sea salts, the neutron irradiated samples are stored for about one month to allow these relatively short-lived interfering radionuclides to decay to tolerable concentrations.

Figure 6 shows that after about 24 days out of the reactor, the ^{24}Na has decayed to insignificant concentrations and ^{82}Br (36 hrs) is now the major gamma-emitting interfering radionuclide. Bromine-82 decays with the emission of a large number of high energy gamma-rays which interfere with the measurement of the trace activation products of interest, and it is necessary to store the samples for another two weeks to allow the ^{82}Br to decay to tolerable levels. High concentrations of ^{35}S and ^{32}P remain in the samples, but they are pure beta emitters and can be tolerated in the gamma-ray spectra. The ^{35}S and ^{32}P are both produced by fast neutron reactions with chlorine-35, as well as by the usual thermal neutron (n,γ) reactions on sulfur and phosphorus. The month-old activated sea salts are then transferred into a constant counting geometry (small polyethylene vials or stainless steel planchets) and counted directly on a Ge(Li) diode detector or a dual coincidence gamma-ray spectrometer (Robertson, et al. 1968). The activated sea salt samples are encased in a thin (0.7 mm thick) lead container to attenuate the low energy bremsstrahlung radiation from the beta-emitters ^{35}S and ^{32}P.

Figure 7 illustrates a typical gamma-ray spectrum of neutron activated sea salts counted on a Ge(Li) detector 54 days after the neutron irradiation, and demonstrates the tremendous resolution advantages of Ge(Li) detectors compared to NaI(Tl) crystals. It is apparent that the eight trace elements, Sr, Rb, Cs, U, Sb, Zn, Fe, and Co, can be measured in sea salts

FIGURE 5

RELATIVE CONCENTRATIONS OF INDUCED RADIONUCLIDES IN SEA WATER FOLLOWING AN INTEGRATED THERMAL NEUTRON EXPOSURE OF 5 x 10^{16} n/cm^2. EMPHASIZING THE PROBLEM OF MEASURING SHORT-LIVED ACTIVATION PRODUCTS IN THE PRESENCE OF HIGH CONCENTRATIONS OF SODIUM-24. BROMINE-82, POTASSIUM-42 AND SULFUR-35.

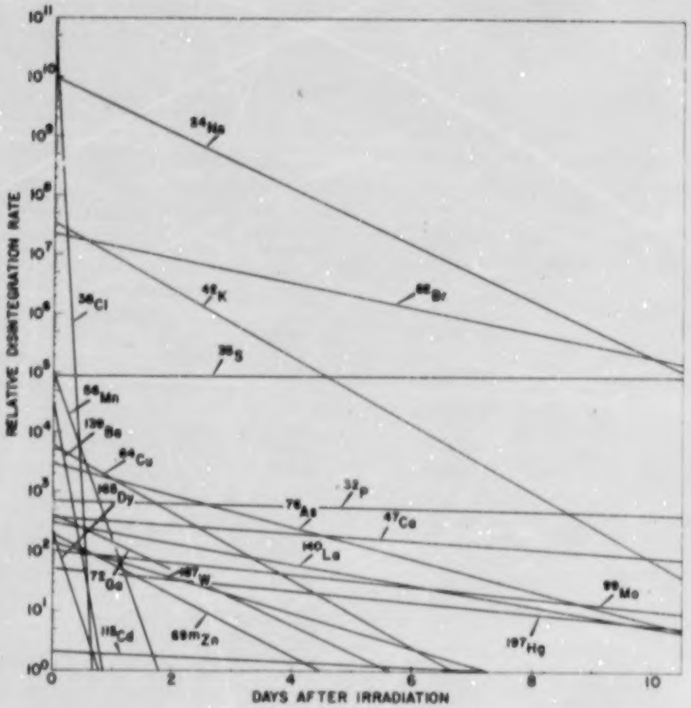


FIGURE 6

RELATIVE CONCENTRATIONS OF INDUCED RADIONUCLIDES IN SEA WATER FOLLOWING AN INTEGRATED THERMAL NEUTRON EXPOSURE OF 10^{18} n/cm^2. EMPHASIZING THE PROBLEM OF MEASURING INTERMEDIATE AND LONG-LIVED ACTIVATION PRODUCTS IN THE PRESENCE OF HIGH CONCENTRATIONS OF SODIUM-24, BROMINE-82, AND SULFUR-35.

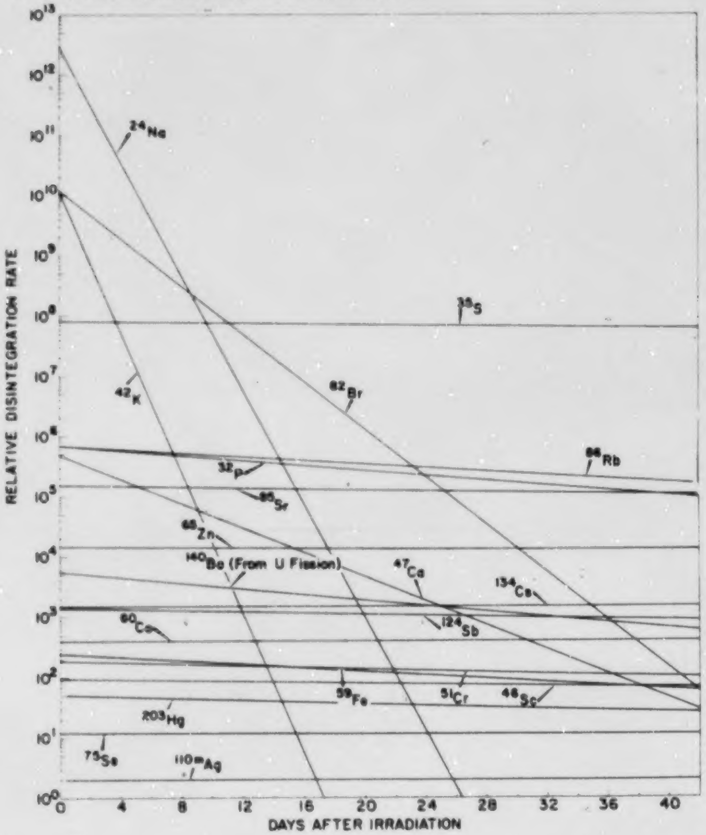
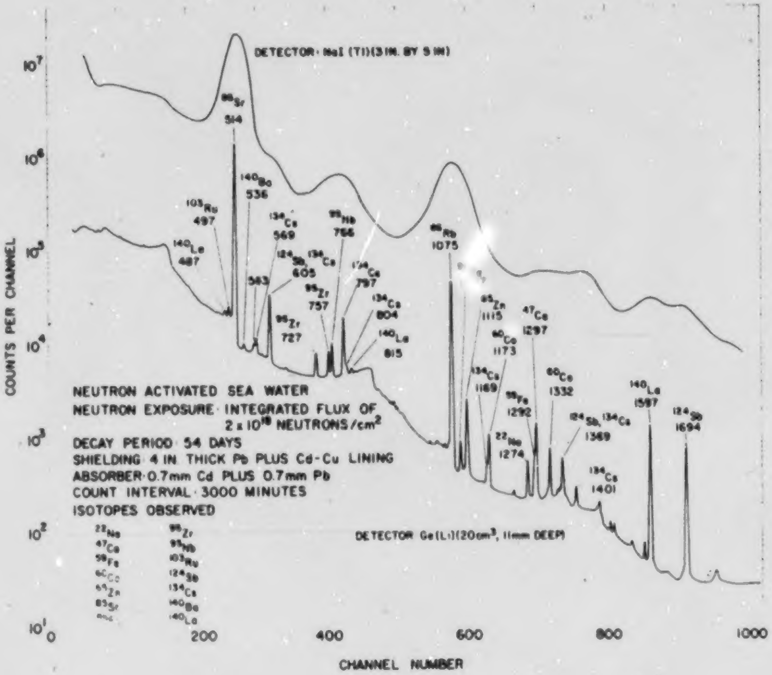


FIGURE 7 *GAMMA-RAY SPECTRUM OF NEUTRON ACTIVATED SEA WATER*



by this technique. Only Sb and Zn are of immediate interest from an environmental pollution concern. Table 2 lists the trace elements in seawater which can normally be measured by INAA and compares the detection limits of this method with the actual oceanic concentrations of the elements observed in seawater. It is obvious that this method is sufficiently sensitive to measure any of the naturally existing concentrations of these elements observed in the oceans.

Mercury can be measured instrumentally in neutron activated sea salts by Ge(Li) diode spectrometry if the samples are irradiated in an extremely thermalized neutron flux. If the neutron flux contains an appreciable fast neutron component, large amounts of the pure beta-emitter ^{32}P are produced by a ^{35}Cl (n,α) ^{32}P reaction. The bremsstrahlung activity from the ^{32}P (maximum beta particle energy 1709 keV) interferes with the sensitive detection of the 279 keV gamma ray from the ^{203}Hg neutron activation product. The Hanford plutonium production reactors, which have now all been closed down, were among the few nuclear reactors in the U.S. which possessed the necessary highly thermalized neutron fluxes. The Triga type of research nuclear reactors, now commonly available throughout the country, do not possess the required neutron flux characteristics necessary for the INAA of mercury in sea salts.

It is often desirable to remove suspended particulate matter from seawater for trace metal analyses, especially in coastal or estuarine waters containing relatively high concentrations of biological and geological material. The techniques for removal and analysis are essentially the same as those described earlier in the section dealing with fresh waters.

Of the pollutant elements of interest only Zn and Sb can be measured in seawater by INAA. However, if preconcentration or postirradiation separations are performed, neutron activation can be used to measure all of the pollutant elements of interest, except Pb and Sn. Table 3 lists the estimated minimum detectable concentrations of the potential pollutant trace

TABLE 2

ESTIMATED DETECTION LIMITS FOR INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS OF SEAWATER*

Element	Typical Oceanic Concentration (μg/l)**	Detection Limit (g/l)
Sr	8000	100
Rb	120	5
Fe	1-20(5)	1
Zn	0.5-10 (3)	0.2
U	3.3	0.1
Cs	0.3	0.003
Sb	0.2	0.005
Hg	0.01-0.3(?)	0.05
Co	0.001-0.1 (0.03)	0.001
Sc	$1\text{-}20 \times 10^{-4}$	1×10^{-4}

* 25 ml seawater; 24-hour irradiation at 10^{13} n/cm^2/sec; 40 days decay; 1000 minute count on 20 cc Ge(Li) diode detector.

** Estimated average concentrations in parentheses.

metals of interest in seawater as measured by both INAA and NAA with separations from interfering radionuclides. These detection sensitivities are compared with the actual observed or estimated naturally occurring concentration ranges for these elements in the ocean. It is obvious that neutron activation with separations possesses the necessary sensitivity to measure all of these trace metals at naturally occurring concentrations well above their detection limits. Some of the necessary preconcentration and/or post-irradiation chemical separation schemes permitting the measurement of these elements in seawater are given below.

2. Analysis of Elements Requiring Preconcentration or Postirradiation Separations

Mercury

Before beginning any of the Hg analytical procedures summarized below, tests for both gain and loss of Hg during storage must be made.

A nearly quantitative loss of both Hg^{++} and methyl Hg chloride from unacidified seawater onto polyethylene storage containers has been observed. The Hg^{++} and methyl Hg chloride, added as ^{203}Hg species, can be kept completely in solution for long storage periods by acidifying the seawater to a pH of about 1.5 with high purity HCl (Robertson, unpublished results, 1972, Battelle-Northwest).

On the other hand, leaching of stable Hg from the walls of acid washed polyethylene distilled water and seawater acidified to pH 1.5 and stored at room temperature has been observed by M. H. Bothner (unpublished results, 1972, Univ. of Washington). The Hg levels of acidified seawater stored in polyethylene at room temperature increased at a fairly steady rate over a 90-day period from .02 to .17 ppb. This effect was not observed on storage of the acidified seawater in hot acid washed pyrex flasks. It is not now known whether leaching of Hg by acidified water samples occurs with all kinds of plastic containers or even for all kinds of polyethylene containers.

Mercury Procedure I

The method of Ljunggren et al. (1971) described previously for analyses of Hg in fresh waters (see Mercury Procedure II in the section on fresh waters) has been utilized to measure Hg in seawater. The procedure is identical to that for fresh waters, except that the neutron irradiated seawater samples must be stored in appropriate shielding until the very intense gamma-radiation resulting from high concentrations of ^{24}Na have decayed to workable levels. However, this procedure is not recommended, since the seawater irradiated in sealed quartz ampoules builds up tremendous pressures from radiolysis products and the quartz ampoules are dangerous to handle.

TABLE 3

ESTIMATED MINIMUM DETECTABLE CONCENTRATIONS OF POLLUTANT ELEMENTS IN SEAWATER BY INAA AND BY NAA WITH SEPARATIONS

Trace Element	Typical Reported Concentrations in Open Ocean (Micrograms/Liter)	Minimum Detectable Concentrations (in micrograms/liter)	
		INAA*	NAA with Separations**
Hg	0.02-0.2	0.05	0.001
Cd	0.06-0.7	16,000	0.001
Ag	0.002-0.05	1.0	0.003
As	2-3	Not Possible	0.0001
Cu	0.5-2	Not Possible	0.002
Cr	0.02-0.6	0.3	0.003
Zn	0.5-10	0.2	0.01
Sn	0.02	Not Possible	9
Se	0.08	0.2	0.02
Sb	0.2	0.02	0.00003

* 25 ml seawater; 24 hour irradiation at 10^{13} n/cm^2/sec; 40 days decay; 1000 minute count on 20 cc Ge(Li) diode detector; based on 3σ above Bkg-Compton contribution in peak areas.

**500 ml seawater; elements chemically separated; 24 hour irradiation at 10^{13} n/cm^2/sec; 3 days decay; 500 minute count on a 20 cc Ge(Li) diode detector; based on twice Bkg contribution in peak areas.

Mercury Procedure II

Weiss and Crozier (1972) developed a preconcentration and post-irradiation separation for measuring Hg in seawater by neutron activation analysis. To 500 ml of filtered, acidified (10 ml conc. HCl per liter of seawater) seawater is added 1 mg of Cu (II) carrier and the Cu is precipitated as the sulfide by bubbling H_2S gas into the seawater for 30 seconds. The Hg in the seawater is coprecipitated with the CuS. The precipitate is collected on a membrane filter, rinsed with high purity water and placed in a 15 ml polyethylene irradiation vial. The walls of the precipitation vessel were washed successively with 5, 3 and 2 ml volumes of nitric acid and the washings were added to the irradiation vial. Blanks were prepared in an identical manner, except high purity water was used instead of seawater. The samples, blanks and appropriate standards (10 ml in 15 ml irradiation vials) are neutron activated for 1 hour in a flux of 2×10^{12} n/cm^2/sec. After irradiation, the sample or blank was quantitatively transferred to a vessel that contained 1 ml of mercury carrier. The solution was brought to pH 1-2 with ammonia liquor and 5 ml of tin (II) chloride were added. The precipitate which formed was isolated by centrifugation. The supernate was discarded and the precipitate was dissolved in 5-10 ml of aqua regia. Copper carrier (1 ml) was added to the solution, the pH was adjusted as above and precipitation with tin (II) was repeated. This precipitate was collected by filtration, and dissolved in aqua regia and the solution was adjusted to pH 7 with ammonia liquor. Hydrogen sulfide gas was bubbled through the solution for 30 seconds. The sulfide precipitate was collected on a Millipore filter and counted.

The irradiated standard Hg solutions after addition of 1 ml of mercury carrier, were precipitated directly as the sulfide and counted.

The 77 keV γ-ray of ^{197}Hg was measured one week after the irradiation with a NaI(Tl) detector coupled to a pulse-height analyzer.

After the radioactivity measurement the mercury sulfide was dissolved in 2 ml of aqua regia and diluted to 25 ml with water. Atomic absorption measurements of this solution were compared to that of a mercury standard to obtain the carrier yield. The yield is 81.1 ± 9.8% for 12 determinations and the sensitivity is 4 nanograms of Hg.

Mercury Procedure III

Robertson (unpublished data, 1972) has developed a very simple neutron activation procedure for measuring mercury in seawater. Seawater samples (stored at pH = 1.5 to prevent Hg losses by adsorption onto container walls) of 200 to 1000 ml are adjusted to pH 3.5 to 8 with NH_4OH, warmed to about 60°C and 20 ml of 1% thionalid is added. The seawater is chilled in a refrigerator and the thionalid crystals (containing co-crystallized Hg) are collected on a membrane filter, washed with high purity water and encapsulated in polyethylene irradiation vials. Blanks are prepared in an identical manner, using high purity water instead of seawater. The samples, blanks and standards are neutron activated for 5 to 8 hours in a flux of about 5×10^{12} n/cm^2/sec. Several weeks after the irradiation the samples, blanks and standards are transferred into new vials and counted in the same geometries on a Ge(Li) diode detector to measure ^{203}Hg. The recovery of Hg is quantitative and the sensitivity is about 5 nanograms.

Silver Procedure I

The same thionalid co-crystallization procedure described above (Mercury Procedure III) is used for determining Ag in seawater, since Ag is also quantitatively co-crystallized from seawater by thionalid. Sensitivity can be improved by directly counting the samples on a dual coincidence gamma-ray spectrometer described in Section V - Gamma-Ray Spectrometry, to measure the multiple coincidence gamma-rays from ^{110m}Ag. The sensitivity is about 0.001 μg Ag/l.

Silver Procedure II

Schutz and Turekian (1965a) have determined Ag in seawater by neutron activating freeze-dried sea salts (from 75 ml of seawater) and appropriate Ag standards for two days in a flux greater than 10^{13} n/cm^2/sec. After several weeks the irradiated salts are dissolved in 25 ml of water and 1 ml of concentrated HCl, silver carrier is added and the solution heated to coagulate the AgCl precipitate. The precipitate is centrifuged, washed with dilute nitric acid and then treated with concentrated nitric acid, diluted with water and then dissolved in ammonium hydroxide. Interfering radionuclides in the solution were scavenged twice by precipitation with ferric hydroxide, and silver was finally precipitated by the addition of nitric acid. It was filtered, dried and weighed as silver chloride. The precipitate was redissolved and ^{110m}Ag measured by gamma-ray spectrometry.

Arsenic Procedure I

Ray and Johnson (1972) report that serious losses (up to 70% in 1 week) occur by adsorption of As from seawater onto polyethylene storage containers, even when the seawater is acidified with 9 ml of concentrated HCl/l of seawater. However, Robertson (1972 unpublished results), using radio-arsenate and arsenite tracers, observed no losses of arsenic from seawater onto polyethylene container surfaces in both acidified and unacidified samples. E. A. Crecelius (1972 unpublished results, U. of Washington) has studied the loss of arsenic added to seawater and lake water as As-74 arsenate. Tests were made with (1) the waters acidified to a pH of 1 with HCl and stored at 20°C, (2) acidified and frozen, (3) unacidified and frozen, and (4) stored unacidified at 20°C. Losses of only 1-14% were found with polyethylene and pyrex containers over a two month period. Portmann and Riley (1964) found polyethylene, pyrex and soda glass absorb 6, 6 and 16%, respectively of arsenate added to unacidified seawater.

Robertson (1972 unpublished work) has measured arsenic in seawater by an $Fe(OH)_3$ coprecipitation technique. To 35 ml of seawater in 50 ml plastic conical centrifuge tubes is added 5 mg of Fe(III) carrier, followed by enough dilute NH_4OH to just precipitate the $Fe(OH)_3$. The precipitate is centrifuged and thoroughly washed twice with two 15 ml portions of high purity water to remove Na and then transferred into small polyethylene irradiation vials and slowly evaporated to dryness. Blanks are prepared in the same manner using 35 ml of high purity water instead of seawater. The samples, blanks and standards are neutron irradiated for 5 to 8 hours in a flux of about 5 x 10^{12} n/cm^2/sec. Two or three days after the irradiation the $Fe(OH)_3$ is dissolved in a 10:1 mixture of nitric-hydrochloric acids and transferred into new counting vials and counted for 10-20 minutes each on a Ge(Li) diode detector to directly measure the ^{76}As 559 keV gamma ray. Some ^{82}Br (554 keV) and ^{122}Sb (564 keV) are present, but are easily resolved by the Ge(Li) detector. The orchard leaf standards are counted on the Ge(Li) detector in an identical geometry to quantify the measurements. The yield is quantitative and the sensitivity is about 0.08 µg As/l.

Arsenic Procedure II

Ray and Johnson (1972) have used the thionalide preconcentration technique to separate As from seawater prior to neutron activation. To 250 ml of seawater is added 1 ml of 5% ascorbic acid and the sample is heated just to boiling. The sample is allowed to cool for 10 minutes and 0.5 ml of ascorbic acid is added and cooled to room temperature. Ten ml of 5N H_2SO_4 is added followed by 2 ml of 2% thionalid in acetone. Stir 5 minutes, wait 10 minutes and then bring solution just to boiling and boil very slowly for 30 minutes to remove acetone. Remove from heat and cool overnight. Collect thionalide crystals (containing co-crystallized As) on membrane filters, rinse with 300 ml of deionized water and encapsule wet filter in a polyethylene vial. Blanks are prepared by using deionized water instead of seawater. The samples, blanks and standards are neutron irradiated for

7 hours in a flux of 10^{12} n/cm^2/sec. One day after the irradiation count the samples, blanks and standards on a Ge(Li) diode detector to measure the ^{76}As 559 keV gamma ray.

Copper Procedure I

Slowey and Hood (1971) have modified the procedure of Rona et al. (1962), for determining inorganic and organic forms of Cu in seawater. The seawater samples are oxidized for 5 minutes by reflux digestion with 10 ml each of 0.1N potassium persulfate and 0.4N H_2SO_4. The solution is cooled, adjusted to a pH of 5.5 to 6.5 and 2 ml of 2% sodium diethyldithiocarbamate in water is added and mixed. Twenty ml of chloroform is added and the solution shaken for 15 minutes to extract Cu. Three extractions are made and the combined chloroform is scrubbed by shaking with high purity water. The Cu carbamate salt is back-extracted from chloroform with three 15 ml portions of 1N HNO_3. The acid solution is evaporated to a small volume, transferred to 1.5 ml polyethylene vials, evaporated to dryness, heat-sealed and neutron activated with appropriate standards for one hour in a flux of 2 x 10^{12} n/cm^2/sec. After neutron activation the copper is separated by sorption on Dowex 1x8 (200 mesh) anion exchange resin from 12N HCl. Interfering radionuclides are eluted from the resin with 12N HCl and then ^{64}Cu and ^{56}Mn are eluted together using 2.5N HCl. The ^{64}Cu and ^{56}Mn in the sample and standards are measured by gamma-ray spectrometry. The method is nearly quantitative and the sensitivity for Cu is 3 x10^{-3} μg.

No other method for measuring Cu in seawater by neutron activation analysis have been reported in the literature, but a convenient method for concentrating Cu from large volumes of seawater is by sorption on Chelex-100 chelating resin (Riley and Taylor, 1968). Copper is quantitatively retained on Chelex-100 at a pH of 7.6 and eluted with 2N HNO_3, and it may be possible to measure Cu without any further separation. If further radiochemical purity is required, a postirradiation separation employing a suitable solvent extraction procedure could be readily accomplished.

Selenium Procedure

The only method for measuring Se in seawater by neutron activation analysis is that reported by Schutz and Turekian (1965b). Seventy-five ml samples of seawater are freeze-dried and the salts and appropriate standards are neutron activated for 2 days in a flux greater than 10^{13} n/cm^2/sec. Several weeks after the irradiation the salts are dissolved in dilute HCl and Se carrier is added. The Se is then precipitated as the sulfide by bubbling H_2S gas into the solution. The precipitate is centrifuged, washed with distilled water, dissolved in HNO_3, and reprecipitated as Se metal by bubbling SO_2 into the solution. The Se is oxidized to SeO_2 with HNO_3, dried and weighed. The SeO_2 is then dissolved in water and brought to a standard volume for counting by gamma-ray spectrometry. Selenium concentrations of 0.05 to 0.1 μg/l were reported using this method.

This method is rather tedious and time consuming and perhaps a more convenient method could be easily developed. Chau and Riley (1965) found that Se(IV) could be coprecipitated from seawater with $Fe(OH)_3$ with ≈ 95% efficiency in pH 4-6 range. Any other forms of Se present in seawater must be converted to Se(IV) for quantitative coprecipitation with the $Fe(OH)_3$.

Chromium Procedures

Schutz and Turekian (1965b) have developed a method for measuring Cr in seawater by neutron activation analysis but the method is tedious and is not recommended as a routine method. Stanford (1971) reported a method based on extraction of Cr(VI) by methyl isobutyl ketone after acidification with hydrochloric acid. For analysis of total Cr, any Cr(III) present is oxidized to Cr(VI) with potassium peroxydisulfate and a copper (II) catalyst. Fukai (1967) and Chuecas and Riley (1966) reported that Cr(III) could be preconcentrated from seawater by coprecipitation with $Fe(OH)_3$. Any Cr(VI) present must be reduced to Cr(III) with sodium sulfite in acid medium to measure total Cr concentrations. The methods of Stanfield (1971) and Fukai (1967) have both used the diverse chemistries of Cr(III) and Cr(VI) in their methods as a measure of the chemical species naturally present in seawater. After Cr has been preconcentrated from a large volume (0.5 to 2 liters) of seawater, the concentrate can be neutron activated and post-irradiation separations as outlined by Pijck (1964) can be performed.

C. Marine Organisms

1. Instrumental Analysis

INAA is particularly applicable for the measurement of trace metals in marine organisms. Approximately 18 trace elements can be measured in most marine organisms by INAA, including the potential pollutant elements Hg, Ag, As, Sb, Zn, and Se (Haller et al., 1969; Morrison and Potter, 1972; Nadkarni and Ehman, 1970; Ranticelli et al., 1969; Robertson et al., 1972). Cadmium and chromium are present in most biological tissues at concentrations just under their INAA detection limits, but can be measured in some specimens when their concentrations exceed about 1 and 0.1 μg/gm dry weight, respectively. The ultimate sensitivities achieved by INAA for many elements are limited by the high concentrations of the pure beta-emitter ^{32}P (14 d) formed in the activated samples. The bremsstrahlung radiation produced from the ^{32}P creates an instrumental dead time problem when biological samples receive too great a neutron exposure.

In practice, the INAA of biological tissue samples consists of encapsuling a 10-1000 mg sample of dried tissue (fresh to dry weight ratios should be obtained) in a cleaned plastic irradiation vial and neutron irradiating the sample and appropriate standards to an integral thermal neutron exposure of about 10^{17} n/cm^2/sec. Sampling and handling procedures for biological tissues during trace element analysis by NAA have been evaluated by Maletskos et al.,(1970). After the irradiation, the samples and standards are transferred into standard counting geometries and counted on a Ge(Li) detector at optimum times following the irradiation to measure both short- and long-lived neutron activated products.

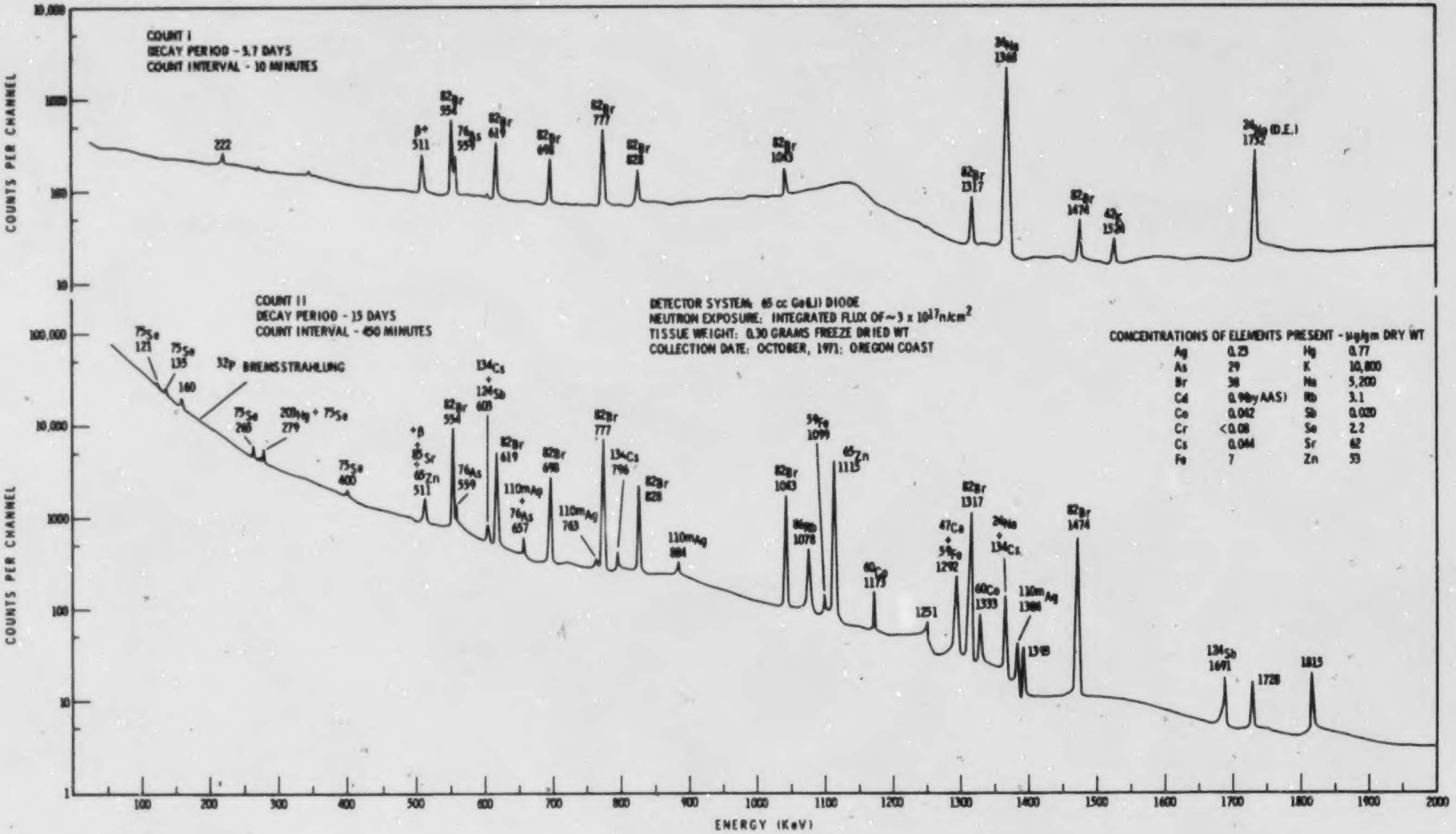
Muscle tissue from two different marine organisms were neutron irradiated and the resulting gamma-ray spectra are shown in Figures 8 and 9. The figures illustrate the neutron activation products which can be measured after both a short and long storage period between the irradiation and counting. The two gamma-ray spectra are similar in many respects, except that Ag, Sr and Sb can readily be detected in the shrimp muscle tissue but not in the sole muscle. The accumulation of Ag, Sr and Sb in these shrimp collected off the Oregon and Washington coast is believed to be due to natural processes and not the result of pollution.

As in the case for natural waters, two to four days out of the reactor the major neutron activation products are ^{24}Na and ^{82}Br, but normally high enough concentrations of ^{42}K and ^{76}As are present for accurate measurements. Some ^{64}Cu is also present, but since some short-lived radionuclides in activated biological tissue are also positron emitters, it is safer to radiochemically separate the ^{64}Cu. When cadmium concentrations in the biological tissue are over about 1 μg/gm dry weight, ^{115}Cd (54 hr) can be instrumentally measured from its 528 keV gamma-ray or the 325 keV gamma-ray from the ^{115m}In isomer.

After the samples have been out of the reactor for about two weeks, most of the ^{24}Na and much of the ^{82}Br have decayed to tolerable levels and a new suite of long-lived neutron activation products can be instrumentally measured, including Rb, Cs, Fe, Zn, Ag, Co, Cr, Hg, Se, Sb and Sc. Table 4 lists the elements which can usually be measured by INAA, and compares their detection limits by this method with the typical concentration ranges normally found in marine biological tissue. As shown in Table 4 the INAA detection limits for most of these elements are sufficiently low to permit their measurement in almost any type of biological matrix. Cadmium, Ag, Cr, and Sb are frequently present in organisms at concentrations near or just below their INAA detection limits, and if necessary, postirradiation radiochemical separations of their neutron activation products can be performed by rather simple group chemical separations.

FIGURE 8

GAMMA-RAY SPECTRUM OF NEUTRON ACTIVATED PINK SHRIMP TAIL MUSCLE TISSUE (IDOE 63)


COUNT I
DECAY PERIOD - 5.7 DAYS
COUNT INTERVAL - 10 MINUTES

COUNT II
DECAY PERIOD - 15 DAYS
COUNT INTERVAL - 450 MINUTES

DETECTOR SYSTEM: 65 cc Ge(Li) DIODE
NEUTRON EXPOSURE: INTEGRATED FLUX OF ~ 3 x 10^{17} n/cm^2
TISSUE WEIGHT: 0.30 GRAMS FREEZE DRIED WT
COLLECTION DATE: OCTOBER, 1971; OREGON COAST

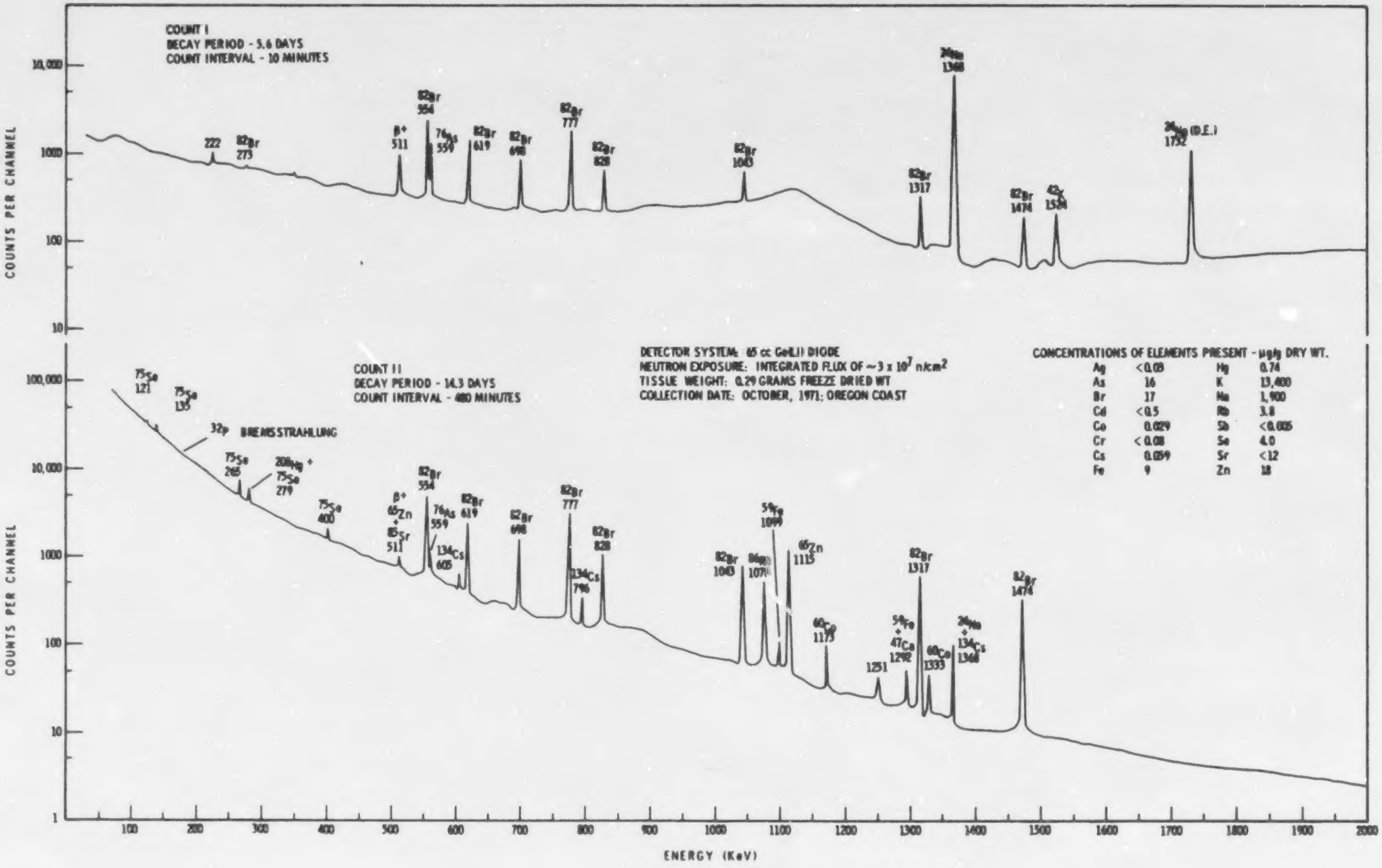
CONCENTRATIONS OF ELEMENTS PRESENT - μg/gm DRY WT

Ag	0.23	Hg	0.77
As	29	K	10,800
Br	38	Na	5,200
Cd	0.9(by AAS)	Rb	3.1
Co	0.012	Sb	0.020
Cr	<0.08	Se	2.2
Cs	0.044	Sr	62
Fe	7	Zn	53

10,000
1000
100
10
COUNTS PER CHANNEL
222
β+ 511
82Br 554
76As 559
82Br 619
82Br 698
82Br 777
82Br 828
82Br 1043
82Br 1317
24Na 1368
82Br 1474
42K 1524
24Na (D.E.) 1732
100,000
10,000
1000
100
10
1
COUNTS PER CHANNEL
75Se 121
75Se 135
160
32P BREMSSTRAHLUNG
75Se 265
203Hg + 75Se 279
75Se 400
+β + 85Sr + 65Zn 511
82Br 554
76As 559
134Cs + 124Sb 603
82Br 619
110mAg + 76As 657
82Br 698
110mAg 763
82Br 777
134Cs 796
82Br 828
110mAg 884
82Br 1043
86Rb 1078
59Fe 1099
65Zn 1115
60Co 1173
1251
47Ca + 59Fe 1292
82Br 1317
60Co 1333
24Na + 134Cs
110mAg 1384
1395
82Br 1474
124Sb 1691
1728
1815
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
1900
2000
ENERGY (KeV)

FIGURE 9

GAMMA-RAY SPECTRUM OF NEUTRON ACTIVATED LEMON SOLE MUSCLE TISSUE (IDOE 59)



COUNT I
DECAY PERIOD - 5.6 DAYS
COUNT INTERVAL - 10 MINUTES

COUNT II
DECAY PERIOD - 14.3 DAYS
COUNT INTERVAL - 480 MINUTES

DETECTOR SYSTEM: 65 cc Ge(Li) DIODE
NEUTRON EXPOSURE: INTEGRATED FLUX OF ~3 x 10^7 n/cm^2
TISSUE WEIGHT: 0.29 GRAMS FREEZE DRIED WT
COLLECTION DATE: OCTOBER, 1971; OREGON COAST

CONCENTRATIONS OF ELEMENTS PRESENT - μg/g DRY WT.

Ag	<0.03	Hg	0.74
As	16	K	13,400
Br	17	Na	1,900
Cd	<0.5	Rb	3.8
Co	0.029	Sb	<0.005
Cr	<0.08	Se	4.0
Cs	0.059	Sr	<12
Fe	9	Zn	18

TABLE 4

ESTIMATED DETECTION LIMITS OF INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS OF BIOLOGICAL MATERIAL (μg/g DRY TISSUE)

ELEMENT	*TYPICAL CONCENTRATION IN MARINE ORGANISMS	DETECTION LIMIT**
Na	500-1500	0.05
K	1000-30,000	20
Rb	0.5-8	1
Cs	0.02-0.4	0.0001
Fe	1-500	2
Zn	10-200	0.5
Br	10-200	0.05
As	<1-50	0.3
Cd	<0.1-10	1
Ag	<0.001-5	0.001
Co	0.001-0.5	0.001
Cr	<0.02-1	0.02
Hg	0.05-5	0.02
Se	0.5-50	0.05
Sb	0.0001-0.05	0.0001
Sc	0.00001-0.002	0.00005

* Typical Ranges in various tissues, with the low ranges usually associated with muscle and high ranges with liver.

** 300 mg of freeze-dried tissue; integral thermal neutron exposure of 3×10^{17} n/cm^2; 20 min. and 1000 min. counts after decay periods of 3 to 5 days and 20 to 30 days, respectively; 20 to 40 cc Ge(Li) diode detection, except where specified.

† Detection limits obtained by dual, coincidence NaI(Tl) spectrometry. Detection limits obtained by Ge(Li) spectrometry for these five elements are approximately 5- to 10-fold higher.

2. Analysis of Elements Requiring Preconcentration or Post-Irradiation Separations

The only elements which cannot routinely be measured in marine biological tissue by INAA are Cd, Cr, Cu and frequently Ag and Sb. However, these elements can be easily measured by neutron activation followed by radiochemical separations.

Cadmium Procedures

Many procedures for determining Cd in biological tissue have been reported: Lieberman and Kramer (1970); Das and de Vries (1971); Livingston et al. (1967); Ljunggren et al. (1971); Edgington and Lucas (1970, 1971); Samsahl et al. (1968); Morrison and Potter (1972).

Biological tissues have been prepared for neutron irradiation in various ways. Some investigators irradiated fresh material, others freeze-dried or ashed samples. Sample decomposition after irradiation has generally been by digestion with H_2SO_4, with $K_2S_2O_8$ or HNO_3 added to speed dissolution. The samples ashed prior to irradiation are dissolved in concentrated HCl.

One Cd separation scheme uses the extraction with dithizone/chloroform solution as the key separation step (Lieberman and Kramer, 1970). Following $H_2SO_4/K_2S_2O_8$ digestion of the samples, the pH is adjusted to 1 to 2 and gross radioactive interferences are extracted into the dithizone layer while Cd stays in the aqueous layer. Subsequently, the pH is adjusted to 13 to 14 and Cd is then extracted into the dithizone layer. Yields are determined by adding ^{109}Cd spike to each acid digestion sample.

Four other separation schemes (Morrison and Potter, 1972; Livingston et al., 1967; Edgington and Lucas, 1970, 1971; Samsahl et al., 1968) use anion exchange as the key to Cd separation. Cadmium forms very strong chloro-complexes which persist until very low HCl concentrations and the complexes are firmly bound to Dowex 1 or 2, or Amberlite IRA-400 anion exchange resins in the Cl form. The great majority of other elements and radioactivities can be eluted from the columns before the Cd. The Cd activity has been measured both on the resin directly and following elution and subsequent precipitation. Samsahl et al. (1968) and Bowen (1967) use several precipitation and dissolution steps involving CdS to remove Cd from interfering isotopes.

Copper Procedure I

Although the 511 keV positron annihilation radiation from ^{64}Cu can usually be detected instrumentally in neutron activation biological tissue, other short-lived radionuclides, including ^{24}Na, are present which also contribute to positron annihilation radiation. Therefore, the ^{64}Cu should be radiochemically separated from interfering radionuclides, principally ^{24}Na. Four general separation schemes have been devised for Cu based on the insolubility of its sulfide, the solvent extractability of its organic chelates, its cation exchange behavior and its electrodeposition properties.

A rapid and simple method developed by Hahn et al. (1968), consists of digesting the biological tissue in nitric acid, dissolving the residue in 4 ml of 1N nitric acid, transferring the solution to a separatory funnel containing 2 ml of 0.1N HCl and extracting ^{64}Cu with 5 ml of 0.01% dithizone in CCl_4 shaking for 2 minutes. The CCl_4 is transferred to a polyethylene counting vial and ^{64}Cu determined by gamma-ray spectrometry.

Copper Procedure II

Bird et al. (1969), have measured Cu in biological tissue by NAA after removal of ^{24}Na by retention on hydrated antimony pentoxide (HAP). The neutron activated tissue sample is digested in fuming HNO_3-H_2SO_4, 0.1 mg of Cu carrier is added and the solution is cooled and passed through a 0.5 gm column of HAP that had been preconditioned with 9N HNO_3. The column effluent (and 9N HNO_3 rinses) is collected and counted to measure ^{64}Cu. Some ^{54}Mn is present, but can be manually stripped from the gamma-ray spectra.

Copper Procedure III

Merlini et al. (1971), measure Cu in biological tissue by NAA after separating ^{64}Cu on columns of cuprous chloride or cupric sulfide. The irradiated tissue sample is digested in hot HNO_3-HF and brought to 6M $HClO_4$ or 1M H_2SO_4 and the solution is passed through a 7 mm diameter by 30 mm long column of cuprous chloride or cupric sulfide. The column is rinsed with 15 ml of the same acid and counted directly by gamma-ray spectrometry. Copper is retained on the column, while most interfering radionuclides are eluted. Only Au, Hg, Sb, Se, Br, W and I are wholly or partially retained on the column, but do not prevent the measurement of the 511 keV ^{64}Cu activity. The counting geometry problems discussed earlier must be considered when counting unusually shaped samples such as these columns.

Copper Procedure IV

Battistone and Lofberg (1970) quantitatively determine Cu in biological tissues by NAA utilizing an electrodeposition technique. The activated samples are digested in HNO_3 in the presence of Cu carrier, and the digest taken just to dryness. The residue is dissolved in 1 ml of concentrated HNO_3 and rinsed into a 25 ml polyethylene beaker with 3 to 5 ml portions of the electroplating solution (10% sodium tartarate, 1% hydrazine hydrochloride, 1% sodium hydroxide, and 0.5% urea, prepared weekly). The Cu is electrodeposited onto cylindrical platinum electrodes at 2.5 volts and an initial current of 2.75 amperes for 45 minutes while stirring with a Teflon-coated magnetic stirring bar. The electrodes are removed from solution while the current is still on and rinsed with 95% ethyl alcohol. The electrodes are then directly counted by gamma-ray spectrometry, or the ^{64}Cu is dissolved off with several ml of 8N HNO_3 which is then counted.

Silver Procedures

Silver can be conveniently separated from neutron activated biological tissue by the method of Merlini et al. (1971). After digestion of the irradiated tissue in hot HNO_3-HF, the solution is brought to 6M $HClO_4$ and passed through a 7 mm diameter by 30 mm long column of cuprous chloride. Over 99% of the Ag is retained on the column, while interfering radionuclides are eluted with 15 ml of the same acid. The column can then be counted directly to measure the ^{110m}Ag by gamma-ray spectrometry. Only Cu, Au, Se, W, I, Hg, Pa, Sn and Sb are wholly or partially retained on the column, but do not interfere with the measurement of ^{110m}Ag. Bromine-82, which is also retained on the column, would normally interfere, but the digestion step with HNO_3 should volatilize most of the Br.

Once the biological tissue sample has been adequately digested by acid dissolution, the same Ag separations as used for seawater can also be employed here.

Antimony Procedure

Antimony can be determined by INAA in most biological tissue by measuring the 1696 keV gamma-ray from ^{124}Sb. The sensitivity for measuring Sb is not limited due to interferences from other neutron activation products, but is limited by the dead-time to the Ge(Li) gamma-ray spectrometer caused by the high levels of the ^{32}P bremsstrahlung. Greater sensitivity could be achieved for Sb if a larger tissue sample were neutron irradiated for a longer time, and the activated tissue sample was encased in some material, such as 0.7 mm thick Pb, to attenuate the ^{32}P bremsstrahlung.

An alternative approach would be to use the rapid separation scheme of Merlini et al. (1970), whereby $^{122-124}$Sb is retained on a cuprous chloride column from 1M H_2SO_4.

Chromium Procedures

After digestion of neutron activated biological tissue samples, Cr may be separated by the solvent extraction procedure described in the section on seawater analysis.

Bowen (1964) has also developed a separation scheme for measuring Cr in biological tissue by NAA. After digestion of the irradiated samples in HNO_3-H_2SO_4 with Cr carrier added, and subsequently with $HClO_4$, the Cr is distilled into 10 ml of water from a $HClO_4$-H_2SO_4 solution to which 0.1 gm of NaCl had been added. The distillation with 2 more portions of NaCl is repeated. The distillate is next transferred to a separatory funnel and shaken with an equal volume of methyl isobutyl ketone, a few drops of concentrated HCl being added to improve the extraction. The aqueous layer is discarded and the organic layer is washed with 2N HCl, and then shaken twice with 10 ml portions of NH_4Cl. The NH_4Cl solutions are scavenged with $Fe(OH)_3$. The supernate is made acidic with acetic acid and treated with 2 ml of barium acetate. The $BaCrO_4$ precipitate is coagulated by boiling, centrifuged and dissolved in hot HCl and reprecipitated at pH 6. The precipitate is washed twice with water, dried, weighed to determine yield and ^{51}Cr is measured by gamma-ray spectrometry.

The above procedure is quite lengthy and Meloni et al. (1969), have measured Cr in biological tissue by removing interfering ^{24}Na and ^{32}P. Tissue samples are digested in HNO_3 and the solution made 1N in HNO_3 and passed through a column of hydrated antimony pentoxide (HAP) to retain ^{24}Na. The effluent (and 1N HNO_3 rinse) is evaporated to about 10 ml and is then passed through a small column of SnO_2 which retains the ^{32}P. The effluent (and 1N HNO_3 rinse) is treated with $KClO_3$ to oxidize Cr(VI) and the solution is passed through a small column of MnO_2 to retain Cr. The MnO_2 is filtered, dried and counted directly to measure ^{51}Cr by gamma-ray spectrometry.

D. Sediments

1. Instrumental Analysis

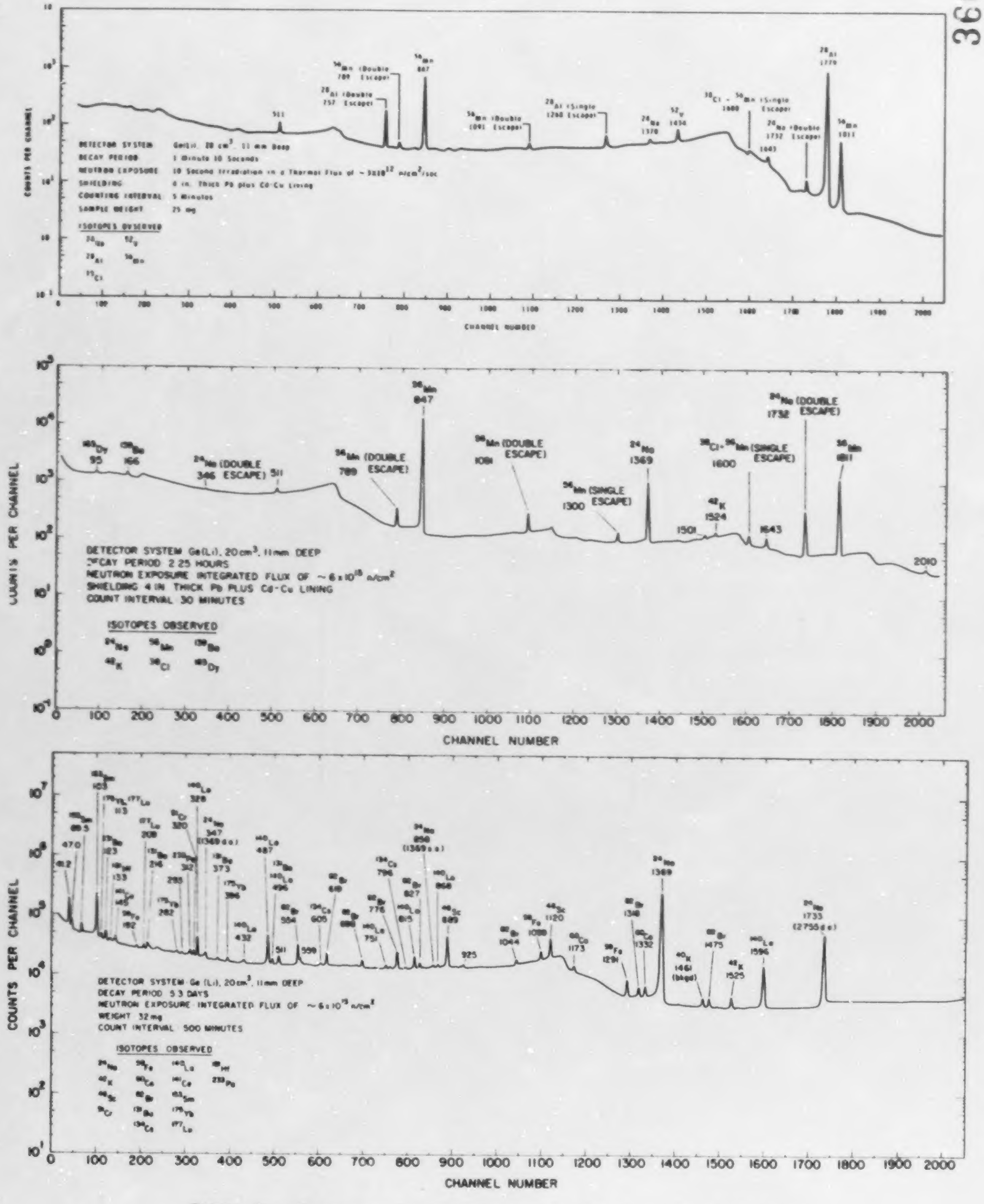
Of the various analytical methods available for the determination of elemental concentrations in geological materials, neutron activation analysis is one of the most sensitive, selective and reliable. INAA, utilizing high resolution Ge(Li) detectors, permits the nondestructive measurement of 25 to 30 elemental constituents in geological material, including marine and fresh water sediments (Brunfelt and Steinnes, 1966; Gordon et al., 1968; Robertson et al., 1972). However, most of the elements which can be measured in sediments by INAA are mainly of a geochemical interest and, of the pollutant metals of concern, only As, Sb and Cr can be measured routinely. Mercury and zinc can be measured instrumentally utilizing a special coincidence-anticoincidence Ge(Li) detector system (Cooper and Perkins, 1972). Utilizing Ge(Li) diode spectrometry and group radiochemical separations, the pollutant elements of interest can be be measured (Filby et al., 1970; Morrison et al., 1969; Peterson et al, 1969).

The general scheme for measuring trace elements in sediments by INAA is to weigh dried sediments (10 to 1000 mg) into cleaned plastic irradiation vials, heat-seal the vials and neutron irradiate the samples, together with appropriate elemental standards encapsulated in an identical geometry as the samples. Elements with short-lived neutron activation products (2.8 minutes to several hours) are measured by irradiating the samples in a rabbit facility for several minutes at a thermal neutron flux of 1 to 50 x 10^{12} n/cm^2/sec, and then counting the samples directly on a Ge(Li) diode detector for 5 to 10 minutes. Elemental standards are identically activated and counted to quantify the concentrations of the elements of interest in the samples. To determine those elements with intermediate half-life activation products (several hours to several days), the identical sediment sample used for the rabbit irradiation, or an aliquot of the same sample, plus elemental standards are neutron irradiated to an integral thermal neutron exposure of about 10^{17} n/cm^2/sec. The samples and standards are then transferred into new counting containers and counted for 10 to 30 minutes on a Ge(Li) diode detector after 2 to 24 hours decay time. For the measurement of elements with long-lived activation products (several days to several years) the samples and standards are recounted 5 to 15 days later for 60 to 200 minutes.

Some typical gamma-ray spectra of neutron activated deep sea red clay obtained by this method are shown in Figure 10. From the rabbit irradiations and short count it is possible to measure the elements Al, V, Mn, Na and Cl. Two to three hours after the long irradiation, the short-lived ^{28}Al and ^{52}V have decayed, and it is possible to measure Na, K, Mn, Cl, Ba and Dy. After a decay period of about 5 days the elements which can be measured are Na, K, Sc, Cr, Fe, Co, As, Br, Ba, Cs, La, Ce, Sm, Yb, Lu, Hf and Th (from ^{233}Pa).

The detection sensitivities for these elements which are obtained by INAA are dependent upon the composition of the sediment sample. For example, evaporite types of sediments having high Na and Br concentrations would create interferences which would limit the detection sensitivities of a number of elements. On the other hand, very pure calcareous sediments would permit more sensitive trace element analysis because of lower concentrations of interfering elements.

In Table 5, estimates of the detection limits for measuring trace elements in typical coastal or deep sea marine sediments by INAA are shown. The detection limits for most of the elements shown in Table 5 were derived by extrapolating from the INAA detection limits for these elements in the standard geological reference materials W-1 and G-2 (Gordon et al., 1968). These standard rocks have trace element concentration ranges somewhat similar to those observed in marine sediments, and this comparison should give detection limits for marine sediments that are reliable to within an order of magnitude. As indicated in Table 5, INAA possessses the necessary sensitivity to instrumentally measure all of the pollutant elements of interest, except Ag, Cd, Cu, Se, Zn and frequently, Hg. The following section outlines methods for the postirradiation separations of the activation products



Gamma-Ray Spectra of Neutron Irradiated Deep Sea Red Clay Sediment after One Minute, Two Hours and Five Days Decay.

TABLE 5

ESTIMATED DETECTION LIMITS FOR THE INAA OF TRACE ELEMENTS IN MARINE SEDIMENTS

Element	Typical Concentration Ranges in Marine Sediments (μg/gm)	INAA Sensitivity* (μg/gm)
Ag	0.01-0.5	0.1
Al	10,000-90,000	10
As	2-20	1
Ba	60-8100	100
Ce	40-70	5
Cd	205	10
Co	1-200	0.1
Cr	10-200	0.8
Cs	0.3-15	0.2
Cu	10-700	1
Dy	0.2	0.1
Eu	0.2-10	0.05
Fe	20,000-60,000	200
Hf	0.1-18	0.1
Hg	0.05-3	0.5
K	3000-30,000	5000
La	2-60	2
Lu	0.2	0.1
Mn	100-10,000	10
Na	2000-40,000	100
Pb	10-200	---
Rb	1-100	1**
Sb	0.5-15	0.1
Sc	0.2-30	0.02
Se	0.1-1	2
Sm	0.5-30	0.3
Sn	0.5-15	500
Sr	200-2000	100**
Ta	0.03-3	0.01
Tb	0.1-7	0.1
Th	0.3-10	0.08
V	10-500	10
Yb	1	0.3
Zn	5-4000	5**
Zr	100-400	70

* 100 to 800 mg of dried sediment; samples irradiated at optimum intervals ranging from 1 minute to 6 hours in a flux of 10^{11} to 10^{13} n/cm^2/sec and counted at optimum intervals after the irradiation for 1 minute to 200 minutes; Ge(Li) diode detectors, 20 cc to 60 cc volumes.

** Determined by counting on a coincidence-anticoincidence shielded Ge(Li) gamma-ray spectrometer (Cooper and Perkins, 1972).

of these elements to give the desired sensitivity for their measurements.

2. Analysis of Elements Requiring Preconcentration or Postirradiation Separations

The only elements of pollution concern which cannot normally be measured in sediments at natural background levels by INAA include Ag, Cd, Cu, Se, Zn and sometimes Hg. Radiochemical separation schemes are given below for these elements.

Mercury Procedures

One important point regardless of the type of post irradiation treatment is that Hg may be lost in drying the sediments--either by freeze drying or oven drying. Preferably, the Hg analysis should be made on the wet sediment, and the wet-dry weight ratio determined on a separate aliquot of the sediment.

Bothner (1972 unpublished data, Univ. of Washington) has used nondestructive INAA to determine Hg levels of 0.5-17 ppm in Bellingham Bay sediments, based on measuring the 279 keV ^{203}Hg gamma ray. However, most sediments will have Hg levels at or below the lower limit of detection by the INAA ^{203}Hg method. Increased sensitivity is achieved by counting the 77 keV gamma rays from ^{197}Hg. However, because of the relatively high concentrations of ^{24}Na activity produced by irradiating marine sediments, the ^{197}Hg must be chemically separated following the irradiation.

The main problem of postirradiation separations of Hg from neutron activated sediments is the dissolution of the samples. Ehmann and Lovering (1967) and Landstrom et al. (1969), point out that fusion of the sediments with Na_2O_2 or Na_2CO_3 is to be avoided, because of loss of Hg before equilibration with the carrier is achieved. The most recommended digestion procedure is with HNO_3-H_2SO_4 in a Bethge apparatus or similar glass container, closed to prevent loss of Hg. However, this method will not dissolve siliceous sediments and digestion with HF must be performed in addition to acid leaching, care being taken not to volatilize Hg during the process.

Following the digestion there is no uniform procedure for the Hg separation but Ehmann and Lovering (1967), Kennedy et al. (1971), and Landstrom et al. (1969), use a key ion exchange step, taking advantage of the strong affinity of Dowex 1 or 2 for chloro-complexes of Hg to bind Hg to the resin while eluting most interfering isotopes. The Hg was subsequently eluted and precipitated as HgS for counting (Ehmann and Lovering, 1967), or electroplated onto Au or Pt foils Pillay et al. (1971), Landstrom et al.(1969), and Ljunggren et al (1970).

An extremely useful summary of extraction, coprecipitation and ion exchange behavior of Hg in different acid solutions is in the monograph by Roesmer (1970).

Cadmium Separations

Once the sediment sample is dissolved by appropriate acid digestion, the general Cd separation procedures outlined in the section of analysis of marine organisms can be used.

Landstrom et al. (1969), Morrison et al. (1969), and Peterson et al. (1969), have outlined sequential group chemical separation schemes for measuring a large number of elements, including Cd, in geological material by NAA. The methods of Morrison et al. (1969), and Peterson et al. (1969), are the same. After dissolution of the sample by H_2SO_4-HF digestions the residue is dissolved in 8N HCl and passed through a column of hydrated antimony pentoxide (HAP) to remove ^{24}Na. The effluent (and 8N HCl rinse) is passed through a column of Dowex 1x8 anion exchange resin which is then washed with 8N HCl. The resin, containing sorbed radiocadmium and radionuclides of Zn, Sb, Re, Ir and Au is counted directly on a Ge(Li) detector to measure ^{115}Cd (54 hr).

Landstrom et al. (1969), treats the irradiated sediment with H_2SO_4-HBr to distill off the volatile bromides of Hg, Sn, Sb, As and Se. The distillate is then digested with HF to complete the dissolution of siliceous material, and the residue is finally dissolved in HCl and passed through two columns of Dowex 2 anion exchange resins in the sulfate and hydroxide forms under various acid concentrations. The Cd is subsequently sorbed onto a column of Dowex 2 anion exchange resin in the sulfate form for counting of the ^{115}Cd by gamma-ray spectrometry.

Copper and Silver Separations

After dissolution of the neutron irradiated sediment by appropriate acid digestion, the Cu and Ag can be separated by the procedures outlined in the sections on analyses of marine organisms and natural waters.

Selenium Separations

Case et al. (1969), described a group chemical separation method for determining Se in geological material by NAA. The irradiated sample is dissolved by H_2SO_4-HF digestion in the presence of carriers and made 6N in HCl and 18N in H_2SO_4. The Se is distilled by dropwise addition of HBr at 220°C, using N_2 carrier gas. The distilled Se is precipitated as the sulfide, which is then dissolved in HCl-HNO_3 and counted by gamma-ray spectrometry to measure ^{75}Se. If further radiochemical purity is required, the procedures given in the sections on natural water analyses could be employed.

Akaiwa (1966), Greenland (1967), and Kiesl (1969) have reported radiochemical separation schemes for measuring Se in meteorites and Wiersma and Lee (1971), and Chau and Riley (1965) described nonradioactive determinations of Se in fresh water and marine sediments. Any of the procedures could be readily adapted to the measurement of Se in marine sediments by NAA.

Zinc Procedures

Zinc cannot routinely be measured in marine sediments, because the 1115 keV gamma-ray from its neutron activation product ^{65}Zn is swamped by the high concentrations of ^{46}Sc, which has a major gamma ray of 1120 keV. Therefore, to measure ^{65}Zn in neutron activated sediments, it needs only to be separated from ^{46}Sc. The sequential separation schemes developed by Morrison et al. (1969), and Peterson et al. (1969), can be used for this purpose. The procedure is exactly the same as that described earlier for measuring Cd in sediments.

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C.5. CONTENTS FOR
AUTOMATED ANALYZERS

1. Laboratory
2. Field
3. References
4. Instrument Notes

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1. Laboratory

Automated analyzers may be employed to determine the metal content of water samples brought to a laboratory, saving both turnaround time and analysis cost. Automation is particularly appropriate when analyzing a number of samples for the same metal. Except for sampling and instrumental set-up, the analysis does not require attention on the part of an operator.

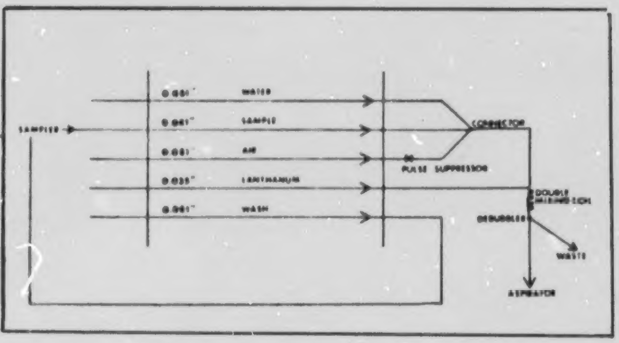


Figure 1. Manifold for automated determination of Ca, Mg, Sr (Ref. 3).

Automation of metals-in-water analysis may be accomplished by coupling modules of a Technicon Auto Analyzer to an atomic absorption instrument (Ref. 1-3). (See Figure 1) In the system used by Fishman and Erdman (Ref. 3), a Technicon sample and proportioning pump was used in series with a Perkin-Elmer Model 303 atomic absorption instrument and Model 165 strip-chart recorder, Figure 1. The method was applied to metals in the ppm-ppb range. Copper, lithium, manganese, potassium, sodium, iron, and zinc were determined by direct aspiration from the sampler; no pretreatment of these samples was necessary. Calcium, magnesium, and strontium, were pretreated by the addition of lanthanum chloride suppressant reagent which the proportioning pump, in the automated system, adds the required volume of suppressant reagent to the samples, mixes the solution thoroughly, and feeds the mixtures to the aspirator.

With either technique, direct or with the proportioning pump, the results are registered on a strip-chart recorder. Depending on the metal, 30-60 samples can be analyzed per hour. Analytical data obtained using this automated system were comparable to data obtained in the usual (manual) manner as shown in Table 1.

Atomic absorption usually measures one metal at a time (some instruments can measure two by using dual lamps), so that a new lamp had to be inserted for each metal. This required about 5-10 minutes. The necessity to change lamps is a disadvantage of the automated atomic absorption method for multielement analysis.

Table 1. (Ref. 3)

A Comparison of Results for Calcium, Magnesium, and Strontium, by Manual and Automated Atomic Absorption Procedures

Calcium mg/l		Magnesium mg/l		Strontium mg/l	
Automatic	Manual	Automatic	Manual	Automatic	Manual
13.4	12.7	2.0	2.1	0.28	0.28
41.0	41.8	35	36	0.81	0.84
13.8	13.3	2.3	2.4	0.09	0.07
85	86	14	15	0.08	0.08
				0.66	0.66

Determination of Lithium with Automatic and Manual Dilutions

mg/l Li	
Automatic	Manual
84	86
178	184
188	192
236	228
288	278
318	306
378	372
422	424
462	464
516	504

Table 2. (Ref. 2)

11. **Printer Output of Automated Mercury Analyses**

Sample No.*	Reading, ppm	Sample No.*	Reading, ppm
0001	00.28	0027	00.26
0003	00.57	0029	00.53
0005	00.88	0031	00.87
0007	01.17	0033	01.21
0009	00.23	0035	00.24
0011	00.59	0037	00.52
0013	00.86	0039	00.90
0015	01.16	0041	01.18
0017	00.23	0043	00.26
0019	00.34	0045	00.50
0021	00.91	0047	00.90
0023	01.20	0049	01.18
0025	00.26		

* Even numbered samples are water blanks. The corresponding readings are all 0.00.

Table II. Results of Duplicate Analyses by Automated Procedure and Comparisons with Manual Procedure

Sample	Hg concentration, ppm		
	I[a]	II[b]	III[c]
Brine 1	0.0077	0.0071	
2	0.0078	0.0076	
3	0.0041	0.0044	
Fish 1	0.07		0.06
2	0.4		0.4
3	0.8		0.6
4	1.2		1.0
Blood[d]	0.055		
	0.062		
Coal[d]	0.48		
	0.45		
	0.50		
	0.52		

[a] I. Automated procedure.
[b] II. Beckman Mercury Vapor Monitor (Industrial Lab).
[c] III. Beckman Mercury Vapor Monitor (Government Lab).
[d] Replicate analyses.

Bailey and Lo (Ref. 2) coupled a Technicon Mark II peristaltic pump to a Varian Techtron Model AA5 for automatic mercury analysis. Modular accessories used with the Model AA5 included an automatic sampler and digital printout. The sample turntable contained 25 samples and 25 water blanks. The automated system is shown schematically in Figure 2. Calibration data obtained by applying the calibration curve technique to water samples of known mercury content covering the range 0.2-1.2 ppm are given in Table 2. Results obtained using the automated and manual procedures for mostly ppb levels of mercury in brine, fish, blood and coal are given in Table 2. Agreement between automated and manual methods ranged between 3-10% for brine samples and 0-30% for fish samples.

Automation of atomic absorption methods for analysis of one metal has an advantage over multielemental atomic absorption analysis because lamps do not have to be changed.

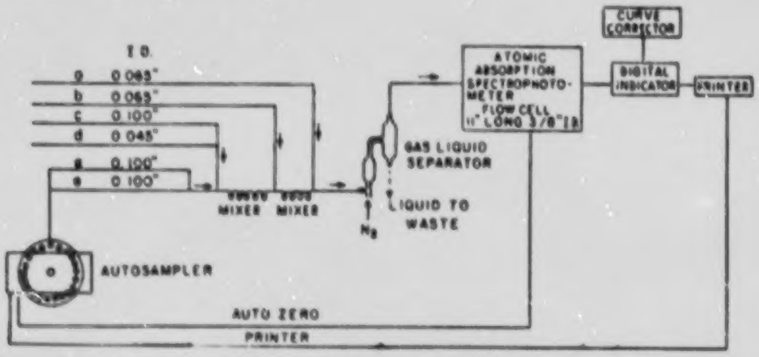


Figure 2. Schematic of equipment used for automatic analysis of mercury (Ref. 2).

a. 10% stannous chloride in 0.5N sulfuric acid
b. 3% hydroxylamine hydrochloride - 3% sodium chloride
c. air
d. 5% potassium permanganate
e. sample

Molecular absorption spectrophotometric methods have sufficient sensitivity to analyze only a few metals in fresh waters. These can include chromium, iron, manganese, calcium, magnesium and strontium. Pre-measurement concentration techniques are required for other elements so that care must be taken to minimize sample loss or contamination.

The United States Geological Survey Laboratory in Salt Lake City, Utah, uses Technicon samplers and pumps to feed samples to atomic absorption instrumentation for trace metals analysis. The laboratory also uses a Coleman 124-D spectrophotometer digital instrument for molecular absorption. About 80-90 determinations may be performed in 20 min using the Coleman 124-D (Ref. 1).

Additional information on automatic analyzers as applied to metals determination in water are found in the excellent papers by Stack (Ref. 2) and Ballinger (Ref. 4), and the text edited by Mancy on Instrumental Analysis for Water Pollution Control (Ref. 5).

2. Field

Continuous analyzers can be used as field monitors for metals in water; they may or may not be portable. Continuous analyzers differ from automatic analyzers primarily in that both sampling, premeasurement treatments, measurement and data reduction are carried out uninterruptedly. Primarily, the sampling is both automatic and continuous for these analyzers.

Continuous analyzers are conceptually the ideal monitors for water quality parameters and constituents. Such instrumentation can be used directly in the field to furnish real-time information concerning the metal content of a particular stream. The method of sampling is important and must be considered in evaluating the analytical data. For example, if a filtering system is included in the sample train, then only the dissolved metal content will be measured. Continuous analyzers for metals are available from manufacturers including Hach, Enviro Control and Technicon to monitor metals including Fe, Cu, and hexavalent chromium. Metal detection is usually by molecular absorption techniques. Mercury monitors based on the flameless vapor method are available from Ionics and Geomet.

The Enviro Control system employs sample filtration by use of two filters in parallel. A flow sensor chamber is used to determine the flow of filtered sample. The amount of flow from the filter is related to the degree of fouling. When the flow is less than a predetermined rate, the sensor electronically activates a three-way ball valve which diverts the sample stream into a clean filter. The fouled filter is removed, cleaned and replaced without interfering with the operation of the filter in service. Air is used to periodically purge the filter to increase the period between filter cleaning. This is accomplished automatically by a cycle timer built into the system.

The Enviro Dual Stage Filter combines the single stage filter with a second stage filtration assembly to reduce particle sizes to 0.45 microns. Microorganisms and finely suspended solids can be removed from the sample stream with this 0.45 μ filter.

Continuous analyzer systems for metals utilize pre-measurement chemical steps which convert all forms of a metal into a single form for subsequent detection. Chemical reactions include complexation, oxidation-reduction, and gasification. Detection may be in terms of the change in intensity of ultraviolet or visible light or as electrical current.

3. References

1. V.T. Stack Jr., "Water Quality Surveillance," Anal. Chem. 44 (8), 32A (1972).

2. F.W. Bailey and F.C. Lo, "Automated Method for Determination of Mercury," Anal. Chem. 43 (11), 1525 (1971).

3. M.J. Fishman and D.E. Erdman, "Automation of Atomic Absorption Analyses," At. Absorption Newslett. 9 (4), 88 (1970).

4. D.G. Ballinger, "Instruments for Water Quality Monitoring," Env. Sci. Tech. 6 (2), 130 (1972).

5. K.H. Mancy, Editor, Instrumental Analysis for Water Pollution Control, Ann Arbor Science Publishers Inc., Ann Arbor, MI 48106 (1971).

4. Instrument Notes

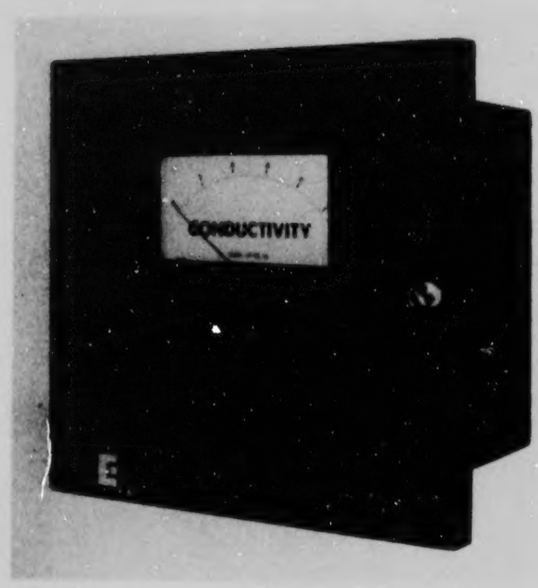
On the following pages are the Instrument Notes for those instruments currently commercially available. The descriptor in the mnemonic identifies the use for metals analysis. The notes are arranged alphabetically by manufacturer, and each model has been assigned a number.

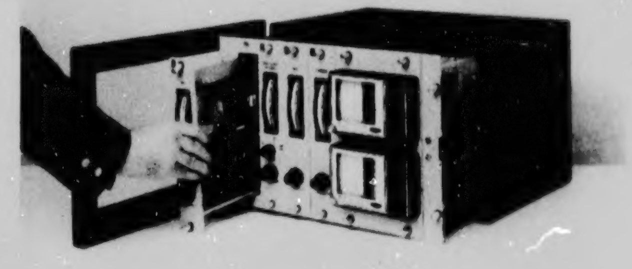
The manufacturer's specifications have been published as available, and we gratefully acknowledge all manufacturers who have assisted in the compilation of their notes. All information has been supplied by the manufacturer, either from brochures and instruction manuals or by private communication with the manufacturer. If no information is given for a particular instrument specification, this indicates that none was available.

The Instrument Notes should not be used as separate entities in themselves. The reader should refer to the discussion preceding the Instrument Notes, the referenced literature, and manufacturers' publications. The technical information in these notes has been compiled from the best available sources and is believed to be correct and up-to-date. These notes will be continually updated, and additional information and comments are certainly solicited.

Simultaneous Multiparameter Monitor

Enviro Control Series 1000 Enviro Monitor





Class	Continuous sensor
Categories of Water	Fresh, Saline, Waste
Principle of Operation	Modular monitoring units, each consisting of a sensor/signal processing/display system
Minimum Detectable Sensitivity	Various, depends on parameter
Range	Various, depends on parameter
Interferences	Varies
Multiparameter Capability	Ammonia, bromide, cadmium, chloride, conductivity, copper, cyanide, fluoride, hardness, iodide, lead, monovalent cation, nitrite, ORP, potassium, sodium, sulfide, suspended solids, dissolved oxygen, turbidity, pH
Sampling	Method: Immerse, flow-through, submersible Volume: 1/4 gpm Maximum Temperature Input: 140°F
Performance	Accuracy: Reproducibility: Linearity: Zero Drift: Span Drift: } Varies depending on parameter

Operation

Ambient Temperature Range: -20° to 130°F
Temperature Compensation: Yes
Relative Humidity Range: 98%
Calibration: Test signal from plug-in module
Procedure: Plug appropriate module into the electronic assembly cabinet, calibrate, and obtain data.
Unattended Period: Varies on application
Maintenance: Varies on parameter

Requirements

Power: 110/220 Vac; battery
Weight: 30 lbs
Dimensions: Cabinet: 27.9 cm x 28.3 cm x 30.5 cm
(11" x 19" x 12")

Features

Output: Meter display, recorder, or telemetry, alarms, controllers
Training: From factory
Options: Alarms, probe chamber, recording

References

a) Manufacturer's bulletin, "Series 1000 Enviro Monitor"
b) Manufacturer's letter of January 30, 1974

Cost

Series 1000 $5,500-$6,000

Remarks

Price depends on configuration of Series 1000.

Address

Gam Rad, Inc.
16825 Wyoming Ave.
Detroit, Mich. 48221
(313) 864-6006
Attn: Mr. Bill Helke

Automatic Water Monitor
Series 2000 Wet Chemical Analyzer

Class	Semi-continuous
Categories of Water	Waste
Principle of Operation	Colorimetric. A metered sample of the water is mixed with a metered amount of reagent to form a colored reaction product. The colored product flows through one absorption cell and the unreacted sample through a reference cell. Light from a single source irradiates both cells, and the difference in attenuation of the light is taken as a measure of the metal being monitored.
Minimum Detectable Sensitivity	0.05-0.2 mg/l (depends on metal being monitored)
Range	
Interferences	Suspended particles (can be filtered out)
Multiparameter Capability	Cr^3, Cu, Fe, Si, Cr^{+6}, alkalinity, PO_4, P, color, hydrazine
Sampling	Method: Continuous Volume: 3.8-11 l/minute (1-3 gal) Maximum Temperature Input: 60°C (140°F) Filter: Optional
Performance	Accuracy: ±5% of full scale Reproducibility: ±5% Linearity: ±5% Noise: ±2% Response Time: 5-30 minutes to 90% of full scale (depends on metal being monitored) Drift: < ±5% full scale/day

Operation

Ambient Temperature Range: 30-100°F
Temperature Compensation: Automatic
Relative Humidity Range:
Calibration: Use known solution, then set meter.
Procedure: Manual or automatic
Unattended Period:
Maintenance: Change reagents
Reagent Consumption: 1.9-19 l/week (0.5-5 gal)

Requirements

Power: 110; 50 Hz
Weight: About 79 kg (175 lb)
Dimensions: 132 cm x 60.9 cm x 20.3 cm
(48" x 24" x 8")

Features

Output: 0-10 mV; 9-100 mV; 0-1 V; 0-5 V
Training: Factory supplied
Options: Alarm, sample handling package

References

Manufacturer's bulletin "Series 2000 Wet Chemical Analyzer"

Cost

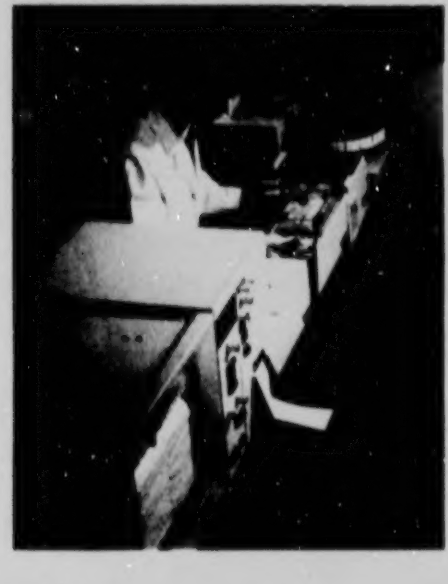
Model 2071 (CU)
Model 2073 (Hexavalent CR)
Model 2074 (Total Soluble CR)
Model 2075 (FE)
Model 2076 (SI)
All Models Base Price $4,000-$7,000

Remarks

Address

Gam Rad, Inc.
16825 Wycming Ave.
Detroit, Mich. 48221
(313) 864-6006
Attn: Mr. Bill Helke

Automatic Multiparameter Monitor
Technicon AutoAnalyzer II



Class	Laboratory batch
Categories of Water	Fresh, Saline, Waste
Principle of Operation	Colorimetric. Samples are aspirated into a sampling line, segmented by air bubbles, and mixed with a reagent stream by dialysis. The resulting colored product is measured by a light source-phototube.
Minimum Detectable Sensitivity	Equivalent to manual method
Interferences	See comparable manual method.

Multiparameter Capability

PARAMETER	TYPICAL RANGE (mg/l except where indicated)	AUTOANALYZER II RATES OF ANALYSIS
Ammonia	0-10	60/hr
Ammonia (seawater)	0-10 μg at /l	60/hr
Nitrate + Nitrite	0-2	40/hr
Nitrate + Nitrite (seawater)	0-45 μg at /l	40/hr
Nitrite	0-1	60/hr
Nitrite (seawater)	0-5 μg at /l	60/hr
Ortho-Phosphate	0-10	50/hr
Ortho-Phosphate (seawater)	0-4 μg at /l	30/hr
Total Inorg. Phos.	0-10	40/hr
Silicate	0-10	60/hr
Silicate (seawater)	0-50 μg at /l	60/hr
Total Soluble Iron	0-10	20/hr
Sulfide (seawater)	0-10 μg at /l	50/hr
Hexavalent Chromium	0-5	40/hr
Copper	0-10	40/hr
Sucrose	0-100	40/hr
COD	0-500	20/hr
Cyanide	0-3	40/hr
Phenol	0-5	40/hr
Fluoride	0-2	20/hr
Hardness	0-300	30/hr
Sulfate	0-300	30/hr
Alkalinity (pH 3 min)	0-500	60/hr
Alkalinity (pH 8 min)	0-100	50/hr
Chloride	0-10	60/hr
Total Kjeldahl Nitrogen	0-100	20/hr
	0-1000	20/hr
Total Phosphorus	0-50	20/hr

Sampling

Method: Semi-continuous
Maximum Temperature Input: 29°C

Performance

Accuracy: Better than analogous manual method
Reproducibility: Better than analogous manual method
Linearity: " " "
Noise: " " "
Response Time: 15 minutes
Zero Drift: Self-compensated
Span Drift: Self-compensated

Operation

Ambient Temperature Range: 13°C - 29°C
Temperature Compensation: Self-compensating
Relative Humidity Range: 10 - 80%
Calibration: Automatic, periodically, with blank and standard solutions
Procedure: Automatic
Unattended Period: Generally no more than 24 hours
Maintenance: Change reagents as needed

Requirements

Power: 117 Vac; 50 to 60 Hz, 11A
Weight: 70 Kg (150 lbs) maximum
Dimensions: (cm)

Module	L	W	H
Sampler IV	38.1	45.7	22.8
Proportioning Pump III	30.5	27.9	22.8
Manifold	43.2	25.6	27.9
Colorimeter	43.2	27.9	33.0
Digital Printer	26.6	39.4	43.2
Recorder	45.7	44.5	45.7

(Inch)

Module	L	W	H
Sampler IV	15	18	9
Proportioning Pump III	12	11	9
Manifold	17	10	11
Colorimeter	17	11	13
Digital Printer	8-1/2	15-1/2	17
Recorder	18	17-1/2	18

Features

Output: Recorder or digital printer
Training: Free at Tarrytown, N.Y.
Options:

SOLIDprep Sampler II	$10,600
On Stream Filter-Sampler	$ 4,500
Continuous Digester	$ 4,800
Continuous Filter	$ 1,530
Analytical Cartridge	$ 330-2,090
Fluoronephelometer	$ 4,815
Flame Photometer IV	$ 6,395
Block Digester, BD-40	$ 2,650

References

Manufacturer's bulletin "AutoAnalyzer II"

Cost

Autoanalyzer II (one channel) $15,155
$22,515 (two channels)
$30,380 (three channels)

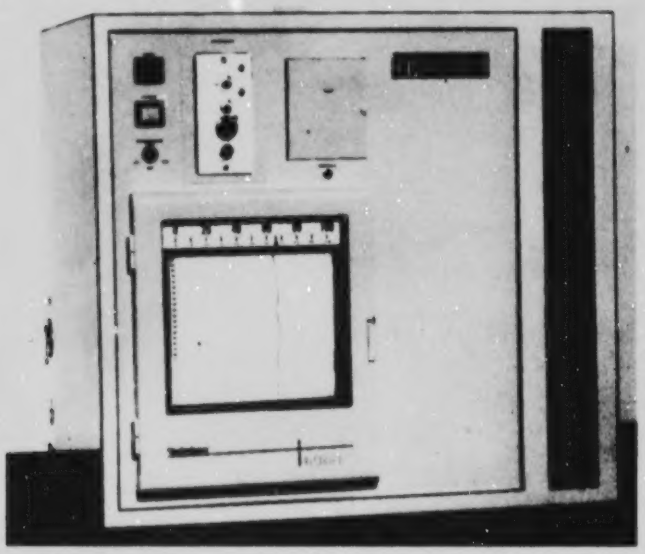
Remarks

Requires a 2' × 8' bench top; many sample ranges available

Address

Technicon Instruments Corporation
Tarrytown, N.Y. 10591
Tel. (914) 631-8000

Automatic Multiparameter Monitor
Technicon Monitor IV



Class	Semi-continuous
Categories of Water	Waste
Principle of Operation	Colorimetric. Sample stream and reagent stream are merged and mixed automatically. Individual samples in the sample stream are segmented by air bubbles. The segmented samples are pumped through a train of modules; each module performs a specific function (e.g., mixing, heating, distillation, color development).
Minimum Detectable Sensitivity	
Interferences	Dissolved color, turbidity

Multiparameter Capability

PARAMETER	TYPICAL RANGE (ml/1 except where indicated)
Ammonia	0-10
Ammonia (seawater)	0-10 µmol/1
Nitrate + Nitrite	0-2
Nitrate + Nitrite (seawater)	0-45 µmol/1
Nitrite	0-1
Nitrite (seawater)	0-5 µmol/1
Ortho-Phosphate	0-10
Ortho-Phosphate (seawater)	0-4 µmol/1
Total Inorganic Phosphate	0-10
Silicate	0-10
Silicate (seawater)	0-50 µmol/1
Total Soluble Iron	0-10
Sulfide (seawater)	0-10 µmol/1
Hexavalent Chromium	0-5
Copper	0-10
Sucrose	0-100
Phenol	0-200 µg/1

Sampling	Method: Continuous Maximum Temperature Input: 29°C Filter: Optional Maximum Number of Sample Sources: 2 (alternately)
Performance	Accuracy: Method dependent Reproducibility: Method dependent Linearity: Method dependent Noise: Method dependent Response Time: 15-60 minutes Zero Drift: Self-compensated Span Drift:
Operation	Ambient Temperature Range: 13°C to 29°C Temperature Compensation: Self-compensated Relative Humidity Range: 10% to 80% Calibration: Automatic; at selected intervals between 2-24 hours, either a wash solution (zero reading) or a standard solution are run through the analyzer. Any adjustment is done automatically. Procedure: Automatic Unattended Period: Generally less than 24 hours Maintenance: Change reagents as needed
Requirements	Power: 110-120 Vac, 60 Hz; 5A maximum Weight: 63.4 kg (140 lb) Dimensions: 57.1 cm H × 62.9 cm W × 47 cm D (22½" × 24¾" × 18½")
Features	Output: Recorder; 0-5 Vdc for telemetry or control Training: Free to employee of purchaser at Tarrytown, N.Y. Options: Continuous filter-sampler
References	(1) Manufacturer's bulletin "Technicon Monitor IV" 1971 (2) "A Significant Advance in the Technology of Industrial Wastewater Montoring", Frederick D. Buggie, 1971. Available from Technicon.
Cost	Monitor IV Basic Instrument $7,400
Remarks	Up to ten sources sampled with special accessories
Address	Technicon Instruments Corporation Tarrytown, N.Y. (914)631-8000

D. METALS

Metals in the aquatic environment are analyzed by a number of instrumental techniques. Although many of the instruments have the capability of analyzing more than one metal in a sample simultaneously, it is usual practice to optimize the analytical procedure for one metal at a time. This is sometimes necessary because of the pre-measurement chemical or separation reactions which focus on one metal in the water sample. Thus, while the instrument is at the center of the monitoring system, the entire system must be considered when evaluating a particular method for analysing a metal.

This section covers instrumentation for each metal; a brief introduction is included which covers uses, manufacturing, toxicity, forms and control of discharges. The reader is referred to Section C for a discussion of the various instrumental methods.

H2O-MET
Contents: AS
June 1973

D.1. CONTENTS FOR
ARSENIC-IN-WATER
MONITORING INSTRUMENTATION

	Mnemonic
A. Introduction	H2O-MET Introduction: AS
1. Characteristics of Arsenic	
2. Forms of Arsenic in Water	
3. Sources and Control of Arsenic in Water	
4. Effects Upon Beneficial Uses	
5. Health Standards	
B. Instrumental Methods	H2O-MET Instrumentation: AS
1. Atomic Absorption	
2. Emission Spectrometry	
3. Molecular Absorption	
4. Polarographic Methods	
5. Other	
C. Summary and Conclusion	H2O-MET Summary: AS
D. Acknowledgment	
E. References	H2O-MET References: AS
F. Table of Selected Instruments	

F. TABLE OF SELECTED INSTRUMENTS FOR ARSENIC-IN-WATER MONITORING

(See H20-MET, Part C, for Individual Instrument Notes)

Principle of Operation	Measured Form	Sensitivity, µg/l.	Multiparameter Capability	Cost $	Remarks
Atomic Absorption					
Bausch & Lomb AC2-20	As	—	Most metals	4,875	Single beam.
Beckman: Model 485	As	700 to 2000	Most metals	5,600	Double beam. Scale expansion to 50×.
Model 495	As	700 to 2000	Most metals	7,345	Double beam. Scale expansion to 100×.
Bendix: Model A1740	As	—	Most metals	—	Single beam.
Model A3000	As	—	Most metals	2,100	Single beam.
Corning Model 240	As	—	Most metals	5,450	Single beam.
E.E.L. Model 140-ER	As	—	Most metals	2,500	Single beam.
Fisher: Dial Atom II	As	2000	Most metals	—	Single beam.
Jarrell-Ash Model 810	As	200	Most metals	—	Double beam, two channel (analyze two metals simultaneously in same sample).
F & J	As	1.0	Hg, Se	150 - 250	Kit for use with atomic absorption instrument.
Hilger-Watts, Model H1170 Atomspek	As	—	Most metals	4,250	Single beam.
Instrumentation Laboratory, Model IL 453	As	100	Most metals	12,500	Double beam, two channel (analyze two metals simultaneously in same sample).
Model IL 353	As	100	Most metals	10,990	Double beam, two channel (see Model 453).
Model IL 253-02	As	—	Most metals	9,660	Double beam, single channel, with turret and background correction.
Model IL 253-01	As	—	Most metals	8,860	Double beam, single channel, with turret.
Model IL 253	As	—	Most metals	8,490	Double beam, single channel.
Model IL 355	As	$*3 \times 10^{-10}$ g.	Most metals	2,995	Flameless, tantalum ribbon, furnace.
Model IL	As	1	Se, Sb	200	Arsine generator system.
Perkin-Elmer, Model 103	As	—	Most metals	3,650	Single beam.
Model 300	As	—	Most metals	7,500	Single beam.
Model 305B	As	—	Most metals	6,950	Double beam.
Model 305BG	As	—	Most metals	—	Double beam. Graphite furnace excitation permanently installed, as is deuterium background corrector.

(cont'd)

TABLE OF SELECTED INSTRUMENTS FOR ARSENIC-IN-WATER MONITORING

(continued)

Principle of Operation	Measured Form	Sensitivity, µg/l.	Multiparameter Capability	Cost $	Remarks
Atomic Absorption					
Perkin-Elmer, Model 306	As	—	Most metals	8,900	Double beam.
Model 403	As	100	Most metals	10,250	Double beam. Integrated readout (average of 10 readings).
Arsine Generator	As	—	Se	275	
Pye-Unicam, Model SP1900	As	220 to 300	Most metals	11,900	Double beam. Lamp turret.
Varian Techtron AA-6	As	600 to 900	Most metals	9,400	
Model 1100	As	150 to 440	Most metals	3,850	
Carbon Rod Atomizer, Model 63	As	20	Most metals	2,995	
Arsine Generator, Model 64	As	1	Se, Hg	50	
Emission Spectrometry					
Instrumentation Laboratory, Model 153	As	10,000	Other metals	—	Nitrous oxide-acetylene flame excitation.
——	As	5	Other metals	—	Laboratory built plasma excitation source (see Ref. 34).
Molecular Absorption					
Beckman ACTA CII	Diethyl-dithio-carbamate	20	Metals, nonmetals	5,760	
Bausch & Lomb, Spectronic 700	Diethyl-dithio-carbamate	20	Metals, nonmetals	2,000	
Polarographic: Differential Pulse					
Princeton Applied Research, Model 174	As(III)	1	Metals, nonmetals	2,000	

A. INTRODUCTION

Arsenic compounds were described and used in antiquity: Hippocrates in the fifth century B.C. recommended the use of arsenic trisulfide for the treatment of skin diseases. Galen and other Roman physicians used arsenic for a variety of conditions including leprosy, tuberculosis, and asthma. During the Middle Ages, arsenic preparations were used extensively by physicians (Ref. 1, 2).

Besides medical uses, arsenic compounds have found use in pesticides, glass fabrication, metallurgy, medical, and veterinarian applications. Some of these compounds and their beneficial applications are summarized in Table A-1 (Ref. 1).

Environmental interest in arsenic and arsenic compounds stems from their toxicity to humans on ingestion and their inflammations caused by skin contact. While beneficial to man in terms of medicinal applications, rodent and pest controls, and manufacturing, residues of arsenic from these uses can be toxic to man, animals, fish and indeed to most living things.

Additional information on arsenic and arsenic compounds can be obtained from The Merck Index (Ref. 1), and from the Encyclopedia of Chemical Technology (Ref. 2).

1. Characteristics of Arsenic

Arsenic can exist in a variety of inorganic and organic compounds in one of three common oxidation states: +3, +5, -3. Only one naturally occurring stable isotope (mass 75) has been observed. Arsenic compounds are widely distributed throughout the earth, with an abundance of about 0.0005% in the earth's crust. A small amount of the metal occurs in the elemental form; the most common minerals are mispickel ($FeAs_2 \cdot FeS_2$), loellingite ($Fe_{2+x}As_{4-x}$), enargite ($3Cu_2S \cdot As_2S_5$), realgar (AsS), and orpiment (As_2S_3). There are over 150 arsenic bearing minerals.

Arsenic is a normal constituent of most soils with concentrations ranging up to 500 mg/kg (Ref. 3, p. 140). The arsenic content of potable waters seldom exceeds 10 μg/l, although values as high as 100 μg/l have been reported (Ref. 4, p. 62).

In the normal course of food consumption, arsenic compounds are constantly ingested. Many foods such as vegetables and fruit contain naturally occurring arsenic, while shellfish may contain over 100 mg/kg. Normal human blood contains 0.2 to 1.0 mg/l of arsenic (Ref. 3, p. 140). However, there is no evidence that arsenic is essential in human nutrition.

Arsenic is found in seawater at a concentration of about 0.003 mg/l, and in marine plants at concentrations up to 30 mg/kg and is highest in the brown algae. It is found in marine animals in the range of 0.005 to 0.3 mg/kg, and is accumulated by coelenterates, some mollusks, and crustaceans. It is moderately toxic to plants and highly toxic to animals (Ref. 6, p. 86).

Pathways of arsenic pollution traceable to man through the ecosystem are complicated by the diversity of forms utilized by man in manufacturing and medicinal applications. Arsenic trioxide, arsenic pentoxide, and cacodylic acid have been used in herbicide applications; waste waters from manufacturers and users of arsenic compounds may produce transient higher concentrations than normal (Ref. 5, 7). Arsenic also occurs as a trace constituent of other consumer products such as phosphate-containing detergents (Ref. 8). These uses can lead to higher levels than background at the source of municipal waste discharges (Ref. 9).

Ferguson and Gavis recently published an excellent review of the arsenic cycle in fresh waters (Ref. 10). Like mercury, arsenic is methylated by certain fungi, yeasts, and bacteria to form gaseous derivatives of arsine: This microbial transformation has not yet been investigated in natural fresh water environments (Ref. 10).

Further information on the characteristics of arsenic may be obtained from the Encyclopedia of Chemical Technology (Ref. 2, p. 711), Water Quality Criteria (Ref. 3, p. 140), and in the paper by Ferguson and Gavis, "A Review of the Arsenic Cycle in Natural Waters," (Ref. 10).

2. Forms of Arsenic in Water

Arsenic exists naturally in the +3 or +5 anionic states in water as inorganic compounds. In fresh waters, it is most often present in the anionic form as either arsenate (+5) or arsenite (+3) (Ref. 11, p. 18). Arsenic in Pacific Ocean water samples was stated to be present mainly as arsenate, and also appears to be present in two New England water sources as arsenate (Ref. 12).

Arsenite (+3) and arsenate (+5) are interconvertible; one form may predominate depending on the pH and oxidizing or reducing conditions of the water. In about 1 M acid

TABLE A-1.

Beneficial Uses of Selected Arsenic and Arsenic Compounds (Ref. 1).

Compound of Arsenic	Uses	
	Manufacturing	Medical
Arsenic	1. Metallurgy for hardening copper, lead, alloys. 2. Manufacture of certain types of glass.	Isotope ^{76}As used as radioactive tracer in toxicology.
Arsenic Disulfide (red) (As_2S_2)	Pigment in painting; in fireworks; tanning and depilating hides; calico printing and dyeing.	
Arsenic Hemiselenide (As_2Se)	Manufacture of glass.	
Arsenic Pentasulfide (As_2S_5)	1. In thin sheets as a light filter. 2. In pigments.	
Arsenic Pentoxide (As_2O_5)	1. Manufacture of colored glass. 2. Wood preservatives. 3. Weed control. 4. As a fungicide.	
Arsenic Trichloride ($AsCl_3$)	1. Ceramic industry. 2. Synthesis of chlorine-containing arsenicals.	
Arsenic Triiodide (AsI_3)		Formerly for chronic dermatitides, various chronic arthroses and certain cases of lymphadenitis and topically as a stimulant in dermatitis.
Arsenic Trioxide (As_2O_3)	Glass, Paris green, enamels, weed killers, metallic arsenic; for preserving hides; killing rodents, insects; in sheep dips; textile mordant.	1. Formerly for dermatitides, chronic bronchitis, asthma, pernicious anemia; topically for skin neoplasms. 2. In veterinary uses: pulmonary emphysema, chronic coughs, anemia, general debility, and chronic non-parasitic skin diseases.
Arsenic Trisulfide (AsS_3)	Glass, particularly infrared transmitting glass; oil cloth, linoleum; electrical semiconductors, photoconductors; pigment; depilating hides; pyrotechnics.	
Arsenious Acid Solution (As_2O_3, HCl, water)		Blood dyscrasias. Veterinarian use: blood diseases, anemia, skin disorders.
Arsenoacetic Acid ($H_2O_3AsCH_2COOH$)		Veterinarian uses: disodium salt used to treat anaplasmosis (babesiasis); as general stimulant in nervous diseases.
Arsphenamine		Formerly as antisyphlitic. Veterinarian uses: formerly used internally in contagious pleuro-pneumonia, petechial fever of horses.
Cacodylic Acid $(CH_3)_2AsO(OH)$		Herbicide. Once used medicinally for various skin conditions.
Arsine (AsH_3)	Used in analytical chemistry to separate arsenic from water sample.	

solutions, the standard electrode potential for the reaction

$$H_3AsO_4 + 2H^+ + 2e = H_3AsO_3 + H_2O$$

is +0.559 volts. Thus, hexavalent chromium, dissolved oxygen, fluorine or chlorine gases oxidize the +3 to +5 form, whereas Sn(II), hydrazine, dissolved SO_2 can reduce the +5 form to +3. In basic solutions, the standard electrical potential falls to -0.67 volts, and it becomes easier to oxidize the +3 form to +5. See Figure A-1.

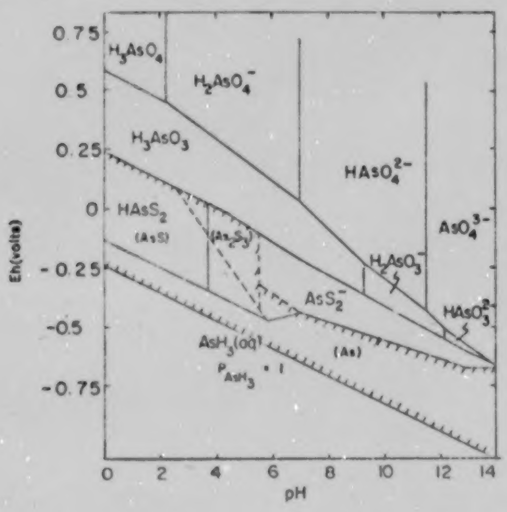


FIGURE A-1. *The Eh-pH diagram for As at 25°C and one atmosphere with total arsenic 10^{-5} mol/l and total sulfur 10^{-3} mol/l. Solid species are enclosed in parentheses in cross-hatched area, which indicates solubility less than $10^{-5.3}$ mol/l (Ref. 10).*

Organoarsenic compounds such as cacodylic acid (hydroxydimethylarsine oxide) are used as herbicides (see H2O-PES section in this Volume). Cacodylic acid is soluble in water to some extent and may be washed into streams or lakes by runoff from land during rainfall. It may be degraded subsequently to an arsine and inorganic arsenite by microbiological action (Ref. 13).

In summary, dissolved naturally occurring arsenic appears to be present primarily as anionic arsenate or arsenite in fresh and saline waters.

3. Sources and Control of Arsenic in Water

Background levels of arsenic in water are probably due to leaching by rainfall and runoff from naturally occurring minerals. Sources traceable to man include herbicides and wastes from industries such as nonferrous metal refining, fertilizer, petroleum refining, and steel works (see Ref. 14).

Arsenic is one of the water constituents included in current reporting requirements for waste water discharges from the fertilizer industry (Ref. 15).

Methods useful for control of the arsenic content of waters include the following: (1) Removal by shaking with <8 mesh granulated Si metal alloys containing 20.5% al, 12.4% Ba, 10.6% Ca, 39.0% Si, and 17.5% Fe (Ref. 16) to reduce 25 μg/l of As (and some other metals) to <1 μg/l; (2) Adsorption into activated carbon after adjustment to the proper pH to reduce levels by approximately 50% for As and some other elements (Ref. 17), and (3) absorption onto precipitated aluminum and iron (III) hydroxides (Ref. 40).

Additional information on sources and control of arsenic in water can be found in the Water section of Chemical Abstracts which is currently published twice each month.

4. Toxicology

The toxicity of arsenic ranges from very low to extremely high depending on chemical form. Metallic (elemental) arsenic and arsenious sulfide are inert or nearly so; on the other hand, gaseous arsine (AsH_3) is extremely toxic. Toxicity of other forms of arsenic, both organic and inorganic, varies between these extremes (Ref. 2, p. 716). Arsenic toxicity is much greater for arsenite, As(III), than arsenate, As(V): These are the forms found most often in waters. Water quality standards do not recognize this distinction, and always are expressed in terms of total arsenic concentrations.

Injurious effects fall generally into three areas: Effects caused by ingestion, inhalation, and skin contact. Ingestion is the most serious.

Following ingestion, the gastrointestinal tract becomes irritated and can degenerate causing nausea, vomiting, diarrhea which may progress to shock and death. Tissues of other internal organs are affected, possibly including nerves. Chronic poisoning can result in exfoliation and pigmentation of skin, induced susceptibility to herpes, polyneuritis, altered hematopoiesis, degeneration of liver and kidneys. Other symptoms of arsenic poisoning include headache, muscular pains, and coma.

Ingestion of 100 mg usually results in severe poisoning and 130 mg has proved fatal. A lethal dose at 325 mg of sodium arsenite was reported (Ref. 3, p. 140). Arsenic accumulates in the body, so that small doses may become fatal in time: A single dose may require ten days for complete disappearance. Chronic arsenosis is of slow onset, and may not become apparent for 2 to 6 years. Small eruptions occur on the hands and on the soles of the feet, sometimes developing into arsenical cancers (Ref. 3, p. 140).

Arsenic compounds, also, are hazardous because of their irritant effects on the skin. Unless protective clothing and gloves are worn, dermatitis may result, particularly in the folds of the skin or moist areas.

Poisoning by means of inhalation of dusts or fumes is unusual. Arsine gas in injurious in 1:20,000 dilution and a few inhalations may cause death from anoxia or pulmonary edema (Ref. 2, p. 718). AsH_3 can cause hemolytic anemia in nonfatal cases. Arsine is a colorless gas with a garlic-like odor which is soluble to the extent of about 20 ml per 100 g of water. It is not particularly stable; decomposition begins to set in well below 300°C. On exposure to light, moist arsine decomposes quickly into the elements, depositing shiny black arsenic.

Arsenic in water can have a deleterious effect on animals. For example, in New Zealand, sickness and death among cattle have been caused by arsenic of natural origin in water supplies (Ref. 3, p. 140). For rats and mice, 96-hour LD_{50} doses of As_2O_3 varied from 15.1 to 214 mg/kg based on oral administration (Ref. 3, p. 141). The lethal dose for animals is believed to be about 20 mg per animal pound (Ref. 3, p. 140).

Fish and other aquatic life have a wide range of tolerances to arsenic. Arsenic trioxide was studied in concentrations of 1.96 to 40 mg/l and found to be harmful to fish or other aquatic life. Work by the Washington Department of Fisheries on pink salmon showed that a level of 5.3 mg/l of As_2O_3 for 8 days was extremely harmful to this species. The same compound at a level of 16 mg/l was found to be quite lethal in 3 to 16 days on mussels. An extensive study on the toxicity of As_2O_3 to many different fish food organisms indicated that important fish food organisms can tolerate an application rate of 2 mg/l of As_2O_3. The amount naturally occurring in the water is generally substantially less (Ref. 6, p. 86).

With respect to lower forms of aquatic life, arsenic concentrations of 3-14 mg/l have not harmed mayfly nymphs, and 10-20 mg/l has been harmless toward dragon and damsel flies. Concentrations of 2-4 mg/l of arsenic are reported not to interfere with the self-purification of streams. Bacteria grow even in the presence of 10,000 mg/l of potassium arsenate, and algae are not killed at 1000 mg/l of arsenate. The fermentation and propagation of yeast are stopped at 300 mg/l of arsenate. (Ref. 3, p. 141)

The potential pollutional hazard to man is stated to be from ingestion of drinking water with high concentrations of arsenic, rather than consuming arsenic containing aquatic organisms (Ref. 10). Although arsenic is greatly concentrated in aquatic organisms, it is evidently not progressively concentrated along a food chain. By contrast with mercury, arsenic when consumed as an organically bound species in flesh evidently has low toxicity (Ref. 10).

Additional information on the toxicity of arsenic may be found in Encyclopedia of Chemical Technology (Ref. 2), The Merck Index (Ref. 1), and Water Quality Criteria (Ref. 3).

5. Health Standards

The 1962 U.S. Public Health Service drinking water standards have a suggested limit that should not be exceeded of 0.01 mg/l arsenic (10 μg/l), with 0.05 mg/l or greater (50 μg/l) constituting grounds for rejection of the water supply. EPA is expected to issue revised standards in 1973. McKee and Wolf list the following limits for arsenic for these beneficial uses:

a.	Domestic water supplies. . . .	0.05 mg/l
b.	Irrigation	1.0 mg/l
c.	Stock and wildlife watering .	1.0 mg/l
d.	Fish and other aquatic life .	1.0 mg/l

The Food and Drug Administration has set a limit of 3.5 mg/kg of arsenic residue on sprayed fruits and vegetables (Ref. 3, p. 140).

Criteria for arsenic in water intended for purposes other than human consumption include the following (Ref. 6):

Irrigation waters, used continuously on all soils -- 1.0 mg/l

Irrigation waters, short term use on fine-textured soil only -- 20 mg/l

The recommended maximum atmospheric concentration of arsenic in dusts, fumes or mists during an 8-hour daily exposure is 0.5 mg/m³; for arsine it is 0.05 ppm (Ref. 2, p. 716).

Additional information on health standards and water quality criteria for arsenic content may be found in Water Quality Criteria (Ref. 6) and Water Quality Criteria, by McKee and Wolf (Ref. 3).

The National Academy of Sciences, Environmental Studies Board, transmitted the manuscript of Water Quality Criteria, 1972 to the U.S. Environmental Protection Agency in March 1973. This is a revision of the 1968 report, Water Quality Criteria (Ref. 6), and is expected to be available in September, 1973.

B. INSTRUMENTAL METHODS

Analyses for arsenic in water are usually performed in the laboratory on grab samples. The arsenic is converted to a single form by chemical means and results are recorded as total arsenic. For samples containing more than one milligram of the metal, arsenic may be determined gravimetrically by precipitation with sulfide, or with silver as the arsenate, or volumetrically by iodometric titration. Its concentration in waters of the United States has a mean value of 64 µg/l, so instrumental methods of analysis are generally used for monitoring purposes.

Methods of analysis for total arsenic in water samples include spectroscopic, electrochemical and activation techniques. Standard Methods, 13th edition (1971), lists two methods: Molecular absorption using silver diethyldithiocarbamate (SDDC) and a mercuric bromide stain method (Ref. 4, p. 62). Standard Methods notes that "successful application of both methods often requires considerable practice." The SDDC method is presently also used by EPA, U.S. Geological Survey and ASTM. EPA also includes an atomic absorption method for arsenic which is not as sensitive as the SDDC method. EPA is investigating a new atomic absorption method for arsenic (Ref. 41).

Arsine generation methods are widely used to separate and/or concentrate arsenic from water samples in absorption and emission spectrometric methods. Reduction of arsenic to arsine is from the +3 oxidation state in acid solution using metallic zinc metal; sodium borohydride at lower acidity is also used. Metals in water that can interfere with arsine generation by zinc plus acid include Cr, Co, Cu, Hg, Mo, Ni, Pt, and Ag. The interference depends upon the concentration of the metals in the particular water sample (Ref. 4, p. 62). In borohydride generation of arsine, 20 µg/l of Ag^+ and Cu^{+2} interfere, while 2 µg/l of these metals do not. A number of other metals do not interfere over the range 2 to 1500 µg/l (Ref. 18). It would seem that users of arsine generation methods should verify the extent of interference in water samples by correlation with other methods such as electrochemical, or by the standard additions method of calibration (Ref. 35).

Whitnack and Martens have cautioned users of the silver diethyldithiocarbamate method to evaluate the extent of interferences of metals in analyzing potable desert water for arsenic content (Ref. 19).

The reader is referred to the H2O-MET section for background information in instrumental methods in general. The following discussions apply primarily to specific analytical methods used for arsenic analysis in water samples, or of potential use for arsenic in water.

1. Atomic Absorption

Atomic absorption methods for arsenic in water include direct aspiration into a flame, arsine vapor flame methods, and flameless techniques. Sensitivity, interferences, and analysis procedure are different for each of these methods. Present activity is centered around more intense sources (electrodeless discharge lamps) and arsine generation methods.

Arsenic may be determined at levels of about 1 mg/l without any concentration steps; solvent extraction and simultaneous concentration extend the lower limit to less than 0.05 mg/l. Parker used a Varian-Techtron AA-5 with a flame from a mixture of hydrogen and air; this provides a highly reducing atmosphere necessary to form elemental arsenic. One problem with the H_2-air flame is the change in optical density of the flame as it fluctuates in thermal and ambient air currents. Interferences encountered include the background absorption and scattering of incident light by flame gases and solution species in the extreme ultra-violet where the most sensitive lines for As are located (193.7 nm and 197.2 nm) (Ref. 20, p. 32).

This background absorption is defined as loss of lamp source intensity due to absorption by substances in the flame other than the element of interest and by light scattering. It is caused by molecular absorption and by light scattering by the solvent or salts in the sample. Background absorption increases with the concentration of the sample solution, and tends to be higher for elements such as As which have their absorption lines in the far UV. As with other constituents, the determination of low levels of arsenic in water tends to expose instrumental limitations.

A fundamental problem at the present time is the extremely short working life of most existing As hollow cathode lamps. At best it is measured in the low tens of hours, and frequently does not extend to two working days. Much difficulty has been reported unofficially in reproducing published results, possibly because the useful life of the lamp has been expended in preliminary work. The problem is compounded because the lamp has a low energy output and energy losses through lamp deterioration or light scattering become very critical. Insufficient data on the new electrodeless discharge lamps is available to judge how well these problems have been solved.

In the method of Fernandez and Manning, the "argon-hydrogen flame" referred to in some of the subsequent descriptions is strictly speaking a misnomer. The flame is hydrogen-entrained air, with argon serving as a carrier gas for the arsine. The flame is supported mainly by the oxygen entrained at the burner surface, and is an especially unstable and sensitive one. It is very sensitive to drafts, and enclosure of the front of the spectrometer has been recommended to avoid fluctuating air currents around the burner. Its stability is also greatly influenced by the rates of flow of hydrogen and argon and it is not surprising that frequently the lamp has begun to deteriorate badly by the time the analyst has mastered control of the variables.

Besides using a blank solution to determine the absorption or scattering losses, a deuterium arc lamp may be used in combination with a rotating chopper mirror. Light from the As hollow cathode lamp or the D_2 arc lamp alternately passes through the flame to the monochromator and detector. Background absorption is normally equal for the beams from both sources, while the element being determined absorbs mainly the resonance light from the hollow cathode source. Data are logged in terms of the ratio of the intensities of the two beams which compensates in large measure for the background absorption (Ref. 21).

Background may also be compensated with a hydrogen filled hollow cathode lamp containing a nickel cathode (Ref. 20, 28). The hydrogen filled tube is said to have an advantage over the deuterium arc in possessing a smaller image size: One comparable to that of the light from the As resonance lamp. The smaller image size permits continuum light to pass through essentially the same portion of the flame as light from the As source so that any variations in other portions of the flame are not focused onto the detector. See Figure B-1 for a schematic of the Instrumentation Laboratory background compensator. It would seem that this approach works most advantageously for a stable flame, i.e., one that may be obtained in a room without air drafts.

Very few chemical interferences are found with the air-H_2 flame. Metals such as Cu and Ni at concentrations of 10,000 mg/l reduce the absorbance by about 8-10%. Addition of nitrogen cools the air-H_2 flame and increases the sensitivity to As. However, the cooler flame also results in a marked increase in interferences from such sources as nitrate, hydroxyl, and chloride ions (Ref. 20, p. 32).

Recommended instrument parameters for As include 7 mA lamp current. Absorbance is reported to be critically dependent on lamp current: Lamps should be allowed to warm up for 30 min in order to stabilize the line-to-background ratio (Ref. 20, p. 32).

Kirkbright, Sargent, and West used a Varian Techtron AA-4 and a flame method utilizing mixtures of air and acetylene, and nitrogen-separated air-acetylene. The lamp source was an electrodeless discharge tube. The air-acetylene flame method is subject to

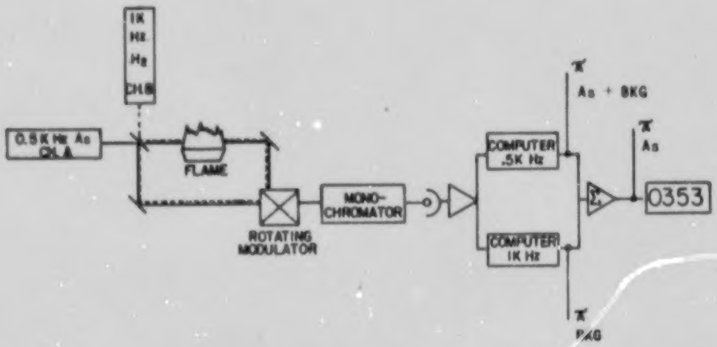


FIGURE B-1. Means by which the signal is corrected (Ref. 28).

TABLE B-1.

Sensitivities and Detection Limits for Arsenic and Selenium (Ref. 23).

Element Wavelength, (nm)	Flame	Burner	Sensitivity, ppm/1% Absorption	Detection Limit, ppm
As 193.7	Air/C_2H_2	Techtron 10 cm	1.2	2.2
	N_2O/C_2H_2	Techtron 5 cm	2.0	1.1
	N_2O/C_2H_2	Beckman 5 cm	2.0	1.8
	N_2O/C_2H_2 (nitrogen-shielded)	Beckman 5 cm	2.0	1.0
Se 196.0	Air/C_2H_2	Techtron 10 cm	1.3	1.3
	N_2O/C_2H_2	Techtron 5 cm	5.0	1.8
	N_2O/C_2H_2	Beckman 5 cm	6.5	2.5
	N_2O/C_2H_2 (nitrogen-shielded)	Beckman 5 cm	6.5	2.0

interferences from metals, including Al, Cr, Mn, Mo, Pb, and Sn: All depress the As absorbance about 8-10%. This flame also has high background absorbance and noise below 200 nm. Surrounding the air-acetylene flame with a flowing nitrogen mantle prevents the access of atmospheric oxygen to the hot interconal zone of the flame and lowers background absorption and noise levels to permit about a threefold improvement in the detection limit (Ref. 22). However, this mantled flame still produced about 30% absorption of the As source radiation at 193.7 nm and 196.0 nm.

One of the more effective flames for As is the premixed nitrous oxide-acetylene mixture. An advantage of this flame is the highly reducing atmosphere in the red feather portion combined with a high temperature to give a lower background absorption below 200 nm. Loss of sensitivity in this hot flame is offset by the lowered background absorption and noise. Also, fewer metals interfere.

Using nitrous oxide-acetylene flame with nitrogen shielding, Kirkbright and Ransom in an excellent paper (Ref. 23) report no interference for 100 mg/l As solution at 193.7 nm at 100-fold weight excesses of the following elements: Al, Ba, Ca, Cd, Co(II), Cr(III), Cu, Fe(III), K, Mg, Mn(II), Na, Ni, Sr, V(IV), Zn, Zr, PO_4(-III), SO_4(-II), NO_3(-I). Of these, Mg, Al, Ca, Fe(III), Co(II), Ni interfere in the air-acetylene flame, and Al, Ba, Ca, Co(II), Fe(III), Mg, Ni, Sr, and PO_4(-III) interfere in the argon-hydrogen flame. The decreased sensitivity in the N_2O-C_2H_2 flame may be offset to some degree by using a multiple pass beam, but this would require a change in the optical system of the instrument.

In their method, atomic absorption measurements were made with a Techtron AA-4 at 193.7 nm using an electrodeless discharge tube source operated at a power level of 35 Watts. The monochromator half-band pass was 0.99 nm. Both Techtron and Beckman-RIIC 5-cm slot burners were employed with the latter equipped to permit operation with or without nitrogen shielding. The shielding gas flow rate employed was 15 liters/min. The nitrous oxide and acetylene flow rates employed were 7.0 and 4.1 liters/min, respectively. The source radiation passed through the red zone of the slightly fuel-rich flame between 2 and 7 mm above the burner head. The sample solution uptake rate was 4 ml/min. Experimental results are shown in Table B-1 for both As and Se.

A high-intensity electrodeless discharge lamp light source also was used by Menis and Rains to help overcome light loss due to absorption and scattering in the determination of As in cast iron and selenium metal (Ref. 24). An argon (entrained-air)-hydrogen mixture was used as the flame. The instrument employed a 0.5 m Ebert mounted monochromator with a grating blazed for 300 nm (3000 Å). The electrodeless discharge lamp was powered by an RF generator from a medical-type diathermy unit which supplied 100 W at 2450 MHz.

Operating conditions are given in Table B-2. The lamp intensity was about two orders of magnitude greater than that obtained from the As hollow cathode lamp (HCL) but was slightly less stable than the HCL (∿5% drift per hour). The detection limit was 0.1 mg/l at 193.7 nm.

TABLE B-2.

Operating Conditions (Ref. 24).

Wavelength, Å	1937
Slit width, μm	100
Light source, electrodeless discharge lamp in (1/4 wave) Evenson cavity	AsI_3
RF power supply, W	50
Burner, Zeiss, multiple pass	3
Oxidant-fuel, Argon (entrained air)	Hydrogen
Scale expansion -- DCR-2	5
Time constant	3
Multiplier phototube, R-106,V	450

Use of the Menis and Rains method required separation of As from the sample matrix. The authors used solvent extraction with diethylammonium diethyldithiocarbamate (DDDC) rather than the customary $AsCl_3$ distillation because recovery of added As in the latter case was found to be only 80-90% of the amount added. Both CH and C_2 radicals interfere at 193.7 nm so that the chloroform ($CHCl_3$) layer cannot be aspirated into the flame. Cu was added to the 2 N HCl extraction solution to displace As from the As-DDDC complex and permit it to be extracted into the HCl layer (Ref. 24).

Another approach directed toward obtaining increased sensitivity for quantitative As determination is based on chemical formation of arsine (AsH_3) gas, followed by sweeping the arsine into a flame using a hydrogen, nitrogen, or argon carrier gas. Separation of As as AsH_3 gas effectively removes sample matrix interferences so that the sensitive hydrogen-air flame combination could be used. Loss of source light intensity due to scattering effects should also be minimized. Introduction of the AsH_3 sample as a "plug" into the flame can increase the sensitivity over that from a solution because all, or mostly all, of the As will be in the flame at the same time.

Holak first applied the concept of As analysis using gasification/collection by converting As to AsH_3 (Ref. 25). The water sample and reagents are placed into an arsine generator flask and the flask quickly connected to a U-tube placed in a liquid nitrogen cold trap through a calcium chloride drying tube. The drying tube is to scrub water vapor from the AsH_3 gas stream: Decomposition of arsine is facilitated in the presence of moisture and light.

After about 30 min, the generator is disconnected, the trap closed with pinch clamps, and the U-shaped tube removed from the liquid nitrogen and allowed to come to room temperature. The arsine is then swept out of the tube by a nitrogen stream into an air-acetylene flame for atomization and detection. The detection limit for this procedure is indicated to be about 0.04 μg (40 ng). The duration of the signal is shorter than that obtained using conventional flame methods so that the instrument response time must be faster (Ref. 25).

In a method described by Madsen, arsine gas, generated by addition of 3 g of 20 mesh granular zinc to a 35 ml water sample containing 0.5 ml 1.6% stannous chloride solution, 0.1 ml of copper sulfate solution and 5 ml of sulfuric acid, is collected in a 0.01 M silver nitrate solution (Ref. 26). The silver ion reacts with the arsine gas to form dissolved As(III) and silver metal. This solution is then aspirated into an argon-hydrogen air flame for detection. Analysis time is about 15 minutes and the necessity to freeze the arsine is eliminated.

Holak's method has been modified by Dalton and Malanoski so that the generated arsine is swept directly into an argon-hydrogen entrained air flame from the generator by excess hydrogen. Advantages include elimination of the freezing step to reduce analysis time and elimination of the need for a carrier gas. Nitric acid or antimony in excess of 0.001 g will interfere with the evolution of the arsine but hydrogen sulfide generated does not. Traces of arsenic in the zinc or other reagents used give a high blank (Ref. 27). The detection limit is 0.10 μg for this method.

Hwang and co-workers used an Instrumentation Laboratory IL-253-02 and applied the arsine generation method followed by direct sweeping into an argon-hydrogen-entrained air flame (Ref. 28). The source was an arsenic hollow cathode lamp, using the line at 193.7 nm. The arsine generator is shown in Figure B-2 and the nebulizer system in Figure B-3.

The nebulizer insert provides argon at the proper flow rate to the inlet of the

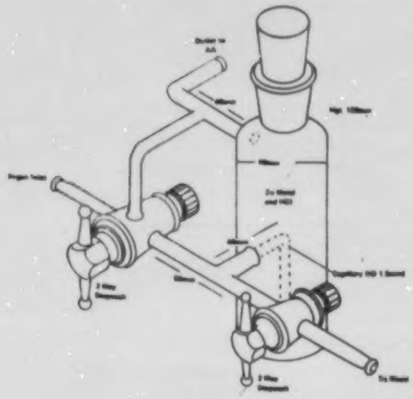


FIGURE B-2. *Arsine generator flask (Ref. 28).*

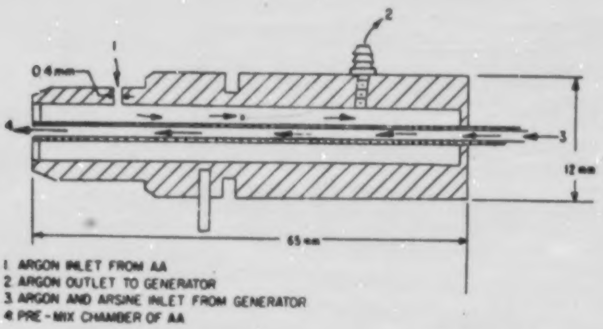

2
1
0.4 mm
4
3
12 mm
65 mm
1 ARGON INLET FROM AA
2 ARGON OUTLET TO GENERATOR
3 ARGON AND ARSINE INLET FROM GENERATOR
4 PRE-MIX CHAMBER OF AA

FIGURE B-3. *Nebulizer for arsine analyzer (Ref. 28).*

generator flask (argon tank pressure is 50 psig; argon instrument setting should be 5 psig). The generator flask has a 3-way stopcock either to bypass or to flush argon through the flask. The 2-way stopcock permits rinsing the flask automatically.

The liquid volume in the generator flask is critical: Above 5 ml the sensitivity is reduced severely. Both blank and sample volumes must be the same to maintain identical reagent concentrations; the volume of reagents added to each must be identical to ensure that any As reagent impurities will have the same concentrations.

For an analysis, 0.3 g of powdered zinc is added to the flask. (For non-acidic solution, rapidly add 1 ml of 6 N HCl.) The flask is immediately stoppered and allowed to sit for 2 minutes. The 3-way stopcock is turned to the flush position and the arsine generated swept into the flame for concentration reading. The flask may then be cleaned by opening the waste stopcock and adding three successive portions of water with a wash bottle. The method was applied to three standard reference materials (SRM) from the National Bureau of Standards: SRM No. 4j (cast iron), SRM No. 7g (cast iron, high phosphorous), and SRM No. 1101 (cartridge brass). Table B-3 shows the good agreement obtained by Hwang and co-workers as compared with the NBS certified values for the As content of these samples.

TABLE B-3.

Accuracy of the Present Method for As (Ref. 28).[a]

SRM No.	NBS Data	Present Method, %
4j	0.030	0.031 ± 0.001
7g	0.014	0.016 ± 0.001
1101	0.009	0.010 ± 0.001

[a] *Instrumentation Laboratory IL-253-02 Instrument.*

The arsine generation method was modified by Fernandez and Manning (Ref. 29), Manning (Ref. 30), and Chu, Barron, and Baumgarner (Ref. 31) to include collection of the arsine gas and excess hydrogen in a balloon using a Perkin-Elmer Model 403 instrument. See Figure B-4. An absolute detection limit of about 0.02 μg was achieved using bulb collection followed by sweeping the arsine into an argon-hydrogen entrained air flame with an argon carrier gas (Ref. 29, 30). Chu, Barron and Baumgarner used an arsine generation and flameless furnace method to obtain about twice the signal output to that obtained using the argon/hydrogen-entrained air flame.

In the bulb-collecting method developed by Fernandez and Manning, 20 ml of water sample containing 0.04-2 μg of As are pipetted into the arsine generator flask (Ref. 29, 30). Sufficient hydrochloric acid is added so that the final solution is 4 N when diluted to a 40 ml volume with deionized water. Any As(V) is reduced to As(III) by adding one ml of a 15% (W/V) potassium iodide solution and mixing the contents well. To this solution, 1 ml of 20% (W/V) stannous chloride

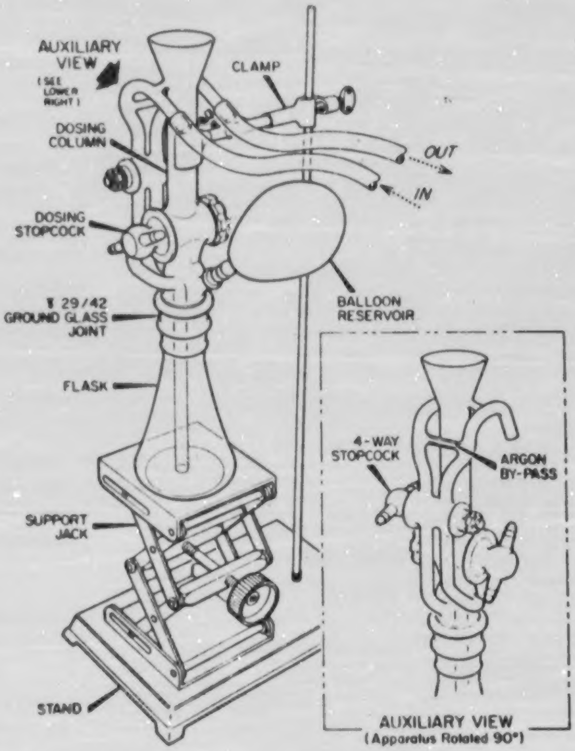

AUXILIARY VIEW
(SEE LOWER RIGHT)
CLAMP
DOSING COLUMN
OUT
IN
DOSING STOPCOCK
₮ 29/42 GROUND GLASS JOINT
BALLOON RESERVOIR
FLASK
4-WAY STOPCOCK
ARGON BY-PASS
SUPPORT JACK
STAND
AUXILIARY VIEW
(Apparatus Rotated 90°)

FIGURE B-4. Perkin-Elmer As/Se sampling system (Ref. 19).

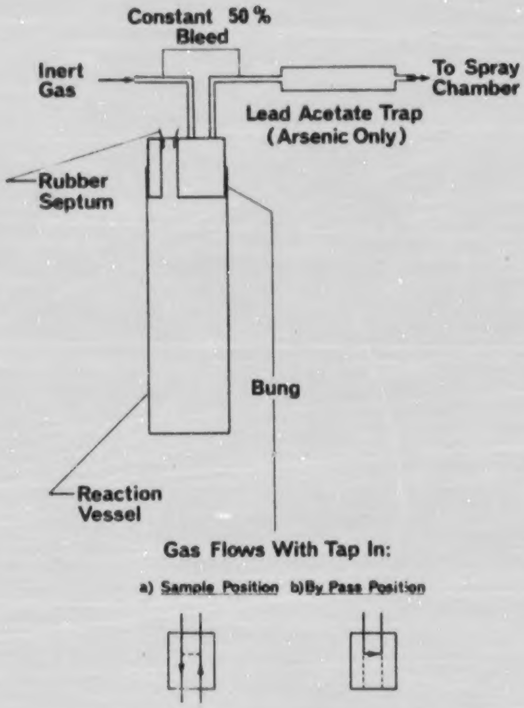

Constant 50% Bleed
Inert Gas
To Spray Chamber
Lead Acetate Trap
(Arsenic Only)
Rubber Septum
Bung
Reaction Vessel
Gas Flows With Tap In:
a) Sample Position
b) By Pass Position

FIGURE B-5. Varian Techtron As/Se apparatus (Ref. 20).

in 8 N hydrochloric acid is added, the flask contents mixed, and the solution allowed to sit for several min. One and one-half g of 20-30 mesh zinc with low arsenic content is added and the balloon collector connected. After 4-5 minutes, argon gas is introduced to sweep the collected arsine into the burner where it is atomized and detected.

Prior oxidation of organoarsenic compounds is necessary before conversion to arsine because they may not be reduced to arsine by zinc and acid. This can be done by wet oxidizing with hot sulfuric/nitric acids followed by heating to fumes of SO_3 then adding ammonium oxalate and heating again to insure removal of residual nitric acid (Ref. 29).

Parker used a Varian Techtron AA-5 together with the apparatus shown in Figure B-5 to generate arsine, followed by introduction of the arsine into a hydrogen-nitrogen air entrained flame (Ref. 20, p. 33). The sample of As was placed in the flask, followed by 1 ml 20% (W/V) stannous chloride and 1 ml 15% (W/V) potassium iodide solution. Acid was added, followed by reaction for at least 10 min. Two ml of zinc slurry (100 g of high purity zinc powder in 100 ml of distilled water) were taken up in a syringe and injected into the generator flask through the septum. The detection limit was 0.002 mg/l As for a 20 ml sample.

Besides the arsine generation and direct methods listed above, direct flameless methods using a tantalum ribbon, graphite furnace, or carbon rod chamber have been used for arsenic measurements. Atomization of the elements is carried out at high temperature (e.g., 2600°C) in an inert atmosphere, such as argon or nitrogen. This step is followed by a sequential process of gradually increasing the chamber temperature during which the sample is sequentially dried, ashed (if necessary), and finally atomized. This time for many types of samples is less than one minute from the insertion of the sample to making the final reading.

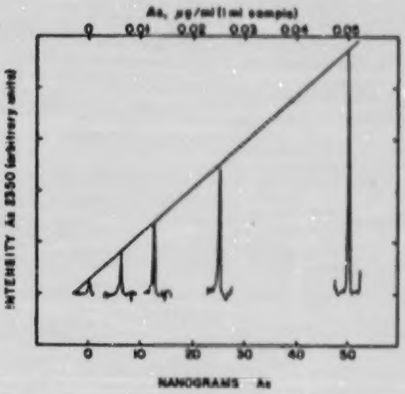


FIGURE B-6. Example analytical curve (from Ref. 34).

Advantages of the direct furnace methods include longer sample residence time in the optical light path, possibility to atomize the entire sample in the furnace, and the possibility with little sample preparation to measure very low concentrations directly. However, the instrument must be able to respond to a rapid change in signal because of the relatively sharp read-out peak as compared to the readout from the flame. Light losses due to scattering or absorption of gaseous substances, salt particles, or smoke from the sample material can also be a problem. This error may be compensable by the use of a continuum source, as discussed for flame atomic absorption.

Twelve elements including arsenic were measured in laboratory prepared standard solutions using a heated graphite furnace (Ref. 32). A Perkin-Elmer Model 403 instrument, equipped with a Model 165 recorder, deuterium background corrector, and a Perkin-Elmer Model HGA-70 graphite furnace, was used. The tube heating electrodes were cooled with a water-jacket and the sample chamber was continuously purged with an inert gas. The sample was placed in the furnace by first removing the window in the metal jacket; then the sample is injected into the center of the furnace with a microliter pipet (see Figure C-18, H2O-MET, Instrumentation, page 16). Sample size can be 5 μ-liters; a larger sample may be used if desired, to increase sensitivity.

The sample solvent is then evaporated by passing a small current to heat the tube and contents. The sample is ashed, if necessary, by increasing the current (and thus the temperature) and finally the temperature is raised to as high as 2600°C to atomize the arsenic. The detection limit for As is 30 μg/l using the furnace, as compared to 500 μg/l, for a flame method (Ref. 32).

In summary, newer methods for As by atomic absorption include separation from the water sample by generation as arsine and use of a flameless furnace. The arsine generation method is subject to interferences from certain metals such as Cr, Co, Cu, Hg, Mo, Ni, Pt, and Ag (Ref. 4, p. 62) and oxidizing agents such as nitric acid. Furnace flameless methods would appear to be more desirable because premeasurement chemical reactions are not required and there is no need for low arsenic containing reagents such as zinc and an acid. However, background corrections for scattering and absorption by smoke, gaseous molecules, and inorganic salts have to be made.

2. Emission Spectrometry

Christian and Feldman used an Instrumentation Laboratory Model 153 and studied parameters for a number of elements including As using emission spectrometry with a nitrous oxide-acetylene flame excitation source (Ref. 33). The detection limit was only 10 mg/l for As; thus this excitation source does not have sufficient sensitivity for most water samples. Using plasma excitation emission, the detection limit is improved to 0.1 to 0.36 mg/l (see H2O-MET, Instrumentation, page 5). Emission spectrometry has the advantage over atomic absorption for As in that the use of a lamp source is not necessary.

Lichte and Skogerboe combined separation of arsenic as arsine with microwave-induced, plasma-excitation emission spectrometry to achieve a detection limit of about 5 ng, or 5 μg/l for a 1 ml sample (Ref. 34). A 2450 MHz microwave generator (Scintillonics Model HV-15) was used with an Evenson quarter wave cavity to induce a plasma in argon at atmospheric pressure. The plasma was contained in a 1-mm i.d. quartz tube. A Jaco Model 8200 0.5 m monochromator was used for the wavelength dispersion, and the intensity at 235.0 nm measured with a phototube. A phase sensitive lock-in amplifier (Ithaco Model 353B) was coupled to an HP 7101B strip chart recorder for data logging. The arsine generator is coupled directly to the plasma excitation source (Ref. 34). In practice, a magnesium perchlorate drying tube was inserted between the plasma and the arsine generator to remove excess water vapor.

Prior to arsine generation, all samples were made 1.5 N in either HCl or H_2SO_4; stannous chloride (4% W/V) was added to reduce any As(V) to the As(III) form. Organic samples were wet ashed with HNO_3/H_2O_2, evaporated to near dryness, and made acidic with 1.5 M HCl. A calibration plot covering the range about 0.005 to 0.05 μg/l is shown in Figure B-6. Analytical data obtained on water, blood, hair and plant samples are shown in Table B-4. The blank amounted to about 2.5 ng. Most of the As in the reagent blank came from the HCl, with zinc being a secondary source. The As in the reagent blank limited the detection limit of this method to about 5 ng.

TABLE B-4.

Comparison of Microwave Emission and

Colorimetric Analysis Results (Ref. 34).

Sample Description	Parts per Million As	
	Microwave Emission	Colorimetry Comparison
Water A	1.32	1.34
B	0.22	0.22
C	0.15	...
D	0.14	...
E	0.09	0.11
F	0.02	...
Blood A (50 ppm added)	52.0	62.0
Blood B	0.22	...
Hair	0.23	...
Plant leaves	9.5	9.5

Braman, Justen and Foreback extended their work on Hg analysis using borohydride reduction to include As and Sb (Ref. 18). The detection limit is near 1 ng and the analysis is rapid (3-6 min elapsed time between sample injection and readout).

For water samples, direct analysis is accomplished by adjusting to a pH range of 7-11. The arsine generator chamber is filled with 25 ml of 1% sodium borohydride and an aliquot up to 10 ml containing 0.005 to 2 μg As is injected through the sample port (Ref. 18). Reaction proceeds for 3-6 min.

Helium carrier gas flowing at a rate of 200 ml/min sweeps the generated arsine gas through a drying tube containing 8 mesh Drierite into a DC discharge chamber where a plasma arc is generated. A power level of 37 watts per lineal inch of discharge is used; the photomultiplier voltage set at 800-900 V; the slit width is 50-100 microns; and the amplifier range is 10^{-6} to 10^{-7} amps. Arsenic spectral intensity is measured at the 228.8 nm emission line. The response is linear for As over the range about 10-45 ng. (Figure B-7.)

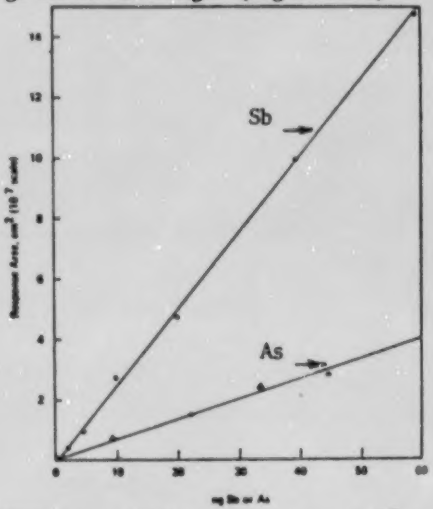


FIGURE B-7. Calibration curves (10^{-7} A amplifier range) (Ref. 18).

Interferences in the method include large amounts of oxidizing agents and other materials which can seriously deplete the concentration of borohydride and those metals at the concentrations indicated in Table B-5. Interfering metals such as Cu and Ag have to be removed prior to analysis by methods such as ion exchange. The organoarsenic compound, cacodylic acid, is not detectably converted to arsine: Organoarsenic compounds may have to be pre-oxidized prior to analysis and subsequently converted to As(III) (Ref. 18).

3. Molecular Absorption

The silver diethyldithiocarbamate (SDDC) method is by far the most widely used colorimetric method for As in water. Other methods include the molybdenum blue (Ref. 12) and mercuric bromide stain (Ref. 4, p. 62). Standard Methods (Ref. 4, p. 62) points out that successful application of the SDDC and mercuric bromide stain methods often requires considerable practice.

The detection limit for the mercuric bromide stain method is 1 μg As, but in general the method should be confined to qualitative or semiquantitative (±5 μg) determinations. Arsenic is gasified as arsine and passed through a column containing mercuric

TABLE B-5.

Interferences in Arsine and Stibine Evolution from $NaBH_4$ Solutions (Ref. 18).

Ion	ppm	Arsenic (0.81 ppm)[a]	Antimony (0.24 ppm)
Ag^+	20	i	i
	2	(–)	(–)
Al^{3+}	20	(–)	(–)
Cd^{2+}	20	(–)	(–)
Cu^{2+}	20	i	i
	2	(–)	(–)
$Cr_2O_7^{2-}$	20	(–)	(–)
Fe^{3+}	20	(–)	i, small amt
	5	(–)	(–)
Hg^{2+}	2	(–)	(–)
Mn^{2+}	20	(–)	(–)
Ni^{2+}	20	(–)	(–)
Pb^{2+}	20	(–)	(–)
Na_2HPO_4	1600	(–)	(–)
Zn^{2+}	20	(–)	(–)

[a] *(–) = no interference at the indicated metal ion concentration. i = inhibits response by 10% or more at 20 ppm metal ion concentration.*

bromide paper. The arsine produces a yellow stain on the paper; the length of the stain is roughly proportional to the arsenic concentration (Ref. 4, p. 62).

In the SDDC method, As is liberated as arsine from the water sample and reacts with a solution of SDDC in pyridine solvent to form a soluble red complex. The intensity of the red color formed is measured using a spectrophotometer and is related to the As concentration using calibration data. The minimum detectable concentration is 1 μg. The reliability of the method has been tested in the following manner: A synthetic sample containing 40 μg/l As, 250 μg/l Be, 240 μg/l B, 20 μg/l Se, and 6 μg/l V in distilled water was analyzed for As by the SDDC method. The relative standard deviation of 46 analyzing laboratories was 13.8%, and the relative error was 0% (Ref. 4, p. 64).

Certain metals such as Cr, Co, Cu, Hg, Mo, Ni, Pt, and Ag interfere in the generation of As. The concentrations of these metals normally present in water samples do not constitute significant interference in the method. Sb may interfere by volatilizing as stibine (SbH_3) and subsequently reacting with SDDC to form a red color. Sulfur, if not too excessive, is scrubbed out by the lead acetate-impregnated glass wool.

Greenberg recently evaluated both the SDDC and mercuric bromide stain methods for the determination of arsenic in some drinking water supplies (Ref. 35). While the accuracy and precision of the two methods leave something to be desired, the methods appear quite capable of distinguishing water samples which exceed the rejection limit of 0.05 mg/l arsenic.

Johnson developed a method for analyzing arsenate (and phosphate) in fresh and ocean waters using the molybdenum blue method (Ref. 12). The method is sensitive to about 0.01 to 0.03 μmole/liter (0.7 to 2.2 μg/l). Arsenate, but not arsenite, forms a blue complex with molybdate so that the method has potential for analyzing these specific forms of arsenic in water. Data for arsenate and phosphate content in two fresh water sources is shown in Table B-6.

A disadvantage of the method may be the 90 min reaction time required to form the arseno-molybdenum complex. Also, the precision of the method will suffer if the phosphate/arsenate ratio is too high inasmuch as the arsenate content is determined as the difference in absorption between (arsenate + phosphate) and phosphate.

TABLE B-6.

Arsenate and Phosphate from Two Freshwater Sources (Ref. 12).

Date	Location	No. Replicates	As(V), μmole	PO_4^{-3}, μmole
8/12/68	Rowe, Mass.[a]	4	0.22 ± 0.33	1.81 ± 0.10
12/23/69	Providence River	3	0.43 ± 0.10	14.1 ± 0.10

[a] *Stream in Davis Mine, an abandoned iron pyrite mine.*

4. Polarographic Methods

Polarography using a dropping mercury electrode in 1 M HCl can distinguish between arsenate and arsenite because arsenate is not electroreduced while arsenite is. Detection limits can be comparable to the atomic absorption methods.

Myers and Osteryoung applied the differential pulse method to analysis of As in various supporting electrolytes (Ref. 36). 1 M HCl was found to be an optimum electrolyte, with a detection limit of about 0.3 μg/l being achievable. Pb(II), Sn(II), Sn(IV), Tl(I), and Tl(III) interfere in the method, but may be accounted for at As concentrations exceeding about 20 μg/l. The method is to obtain a current-voltage curve, then oxidize As(III) to the polarographically inactive As(V) form with Ce(IV), and obtain another polarogram. The arsenic signal is the difference between the two polarograms at the As(III) peak potential. As(V) may be determined by reducing to As(III) with a hydrazine salt, SO_2 gas, acidic KI, or by Cu(I) reduction and benzene extraction, followed by back extraction into water.

Polarograms were obtained using a Princeton Applied Research Model 174 Polarographic Analyzer, with a Model 174/70 drop timer. The capillary had a mercury flow rate of 2.50 mg/sec at open circuit in 1 M HCl and a mercury column height of 48.0 cm. The mercury electrode drop time was 5.73 sec under these conditions. The cell used was a 100 ml Berzelius beaker fitted with a Leeds and Northrup 067513 polyethylene top containing a gas tube for sparging, a 0.635 cm (1/4 in.) diameter carbon rod counter electrode, and a Beckman Model 391-70 saturated calomel reference electrode. As(III) aliquots were pipetted into the cell, the solution sparged with nitrogen, and polarograms recorded. See Figure C-11, H2O-MET, Instrumentation, page 10. In 1 M HCl solution, for thirteen replicate runs at concentrations of 1.93 μg/l (2.4×10^{-8} M) As(III), the relative standard deviation was 16.4%. Six runs at 19.3 μg/l (2.4×10^{-7} M) had a relative standard deviation of only 1.4%. The very good sensitivity attainable is indicated by the detection limit of 0.22 μg/l at the 95% confidence level. Calibration data covering a concentration range of four orders of magnitude are shown in Table B-7 (Ref. 36).

The method has been applied to arsenite determination in unfiltered-activated sludge and is being applied to investigate the oxidation state of arsenic in microbiological systems (Ref. 36).

In summary, the polarographic differential pulse method is sensitive and capable of differentiating As(III) and As(V) forms of arsenic in 1 M HCl. The reliability of the technique for field applications has not yet been established.

TABLE B-7.

i_p/C vs. Concentration (Ref. 36).

C(M)	i_p(μA)	i_p/C(μA/mM)
3.45×10^{-8}	0.0117	340
3.45×10^{-7}	0.1175	341
3.45×10^{-6}	1.188	345
3.45×10^{-5}	10.4	302
3.45×10^{-4}	104	302

5. Other

Ray and Johnson applied neutron activation analysis to arsenic determination in freshly collected natural waters at the 0.3 - 3.4 μg/l level (Ref. 37). In the method, As(V) in more than 250 ml water samples was reduced to As(III) with ascorbic acid and precipitated with thioanalide. The precipitate was collected on 0.45 μm membrane filters, placed in 1.8 ml polyethylene vials and irradiated with thermal neutrons at a flux of 4×10^{12} n/cm²/sec for 7 hours. After cooling for 12 hours, the gamma activities of ^{76}As were counted at the 0.559-MeV peak for 100 sec, using a Ge(Li) detector. Recoveries of 1.94 - 19.7 μg/l As(V) and of 3.96 - 13.8 As(V) added to six sea water and five deionized water samples, respectively, were quantitative with an average error of 0.15 μg/l. The As values determined in 11 water samples including rain, estuarine, sea, and tap water were found to be 0.3 to 3.4 μg/l.

Gilmore applied an x-ray fluorescence method to the determination of triphenylarsine in benzene of C_{11} to C_{14} paraffin solvents (Ref. 5). Depending on the thickness of zinc filters used, the detection limit was 0.17 to 0.46 ppm. The method was applied to determination of As in three oil samples; results compared favorably with those obtained by neutron activation (NA). See Table B-8.

TABLE B-8.

Determination of Arsenic in Oils (Ref. 5).

Sample	ppm As, X-Ray	$\sigma_{x\text{-ray}}$, ppm	ppm As, NA
A	0.42	0.10	0.40
B	4.19	0.13	5.5
C	36.2	0.6	37.6

C. SUMMARY AND CONCLUSION

In summary, total arsenic in water samples is converted to arsine and analyzed primarily using the silver diethyldithiocarbamate (SDDC) molecular absorption method according to present water quality procedures. The more recent atomic absorption and plasma emission methods using arsine generation have a lower detection limit than the SDDC method. The differential pulse polarographic method combines a low detection limit, good turnaround time, and the ability to differentiate arsenate and arsenite forms.

Flame atomic absorption methods involving arsine generation from the sample are sensitive and fast but are subject to interferences such as loss of incident light intensity due to flame absorption and oxygen (in air) interference. High intensity electrodeless discharge lamps can be used as light source to compensate for attenuation in intensity due to flame absorption. The recently announced Perkin-Elmer electrodeless discharge lamps may give almost twice the absorbance as hollow cathode lamps in an air-acetylene flame. See Figure C-1 (Ref. 39). The detection limit for As using an electrodeless discharge lamp source in combination with a flameless graphite furnace is reported to be 0.2 µg/l in a 100 microliter sample (Ref. 39).

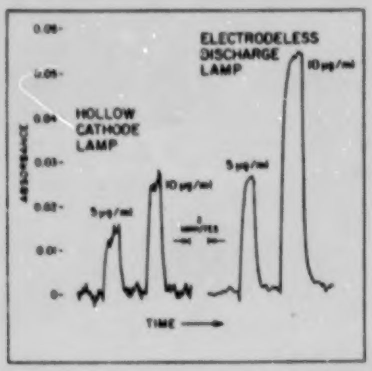


FIGURE C-1. Determination of 5 and 10 µg/ml arsenic with a hollow cathode and an EDL, in an air-acetylene flame (Ref. 39).

The two inorganic forms of arsenic likely to occur in water are differentiated using differential pulse polarography, molecular absorption spectrophotometry using molybdenum blue, or by arsine generation methods using zinc in which As(III) forms arsine but As(V) apparently does not.

More intense and stable light sources are needed for As analyses using flames to compensate for flame absorption/scattering losses (Ref. 38).

In conclusion, there certainly appears to be room for improvement in arsenic-in-water methodology. For example, the specificity of the arsine separation and concentration step could be improved. One approach that may have merit is to take advantage of the electrochemical reduction of As(III) to arsine at mercury electrodes (see Ref. 36). In 1 M HCl, arsine is formed from As(III) at an applied potential centering around -0.8 volts vs a saturated calomel reference electrode. A large area mercury pool cathode could be used and the solution agitated by a Teflon covered magnetic stirrer and by bubbling a stream of hydrogen or other appropriate gas through the solution. The generated arsine would then be swept by the hydrogen gas stream into a gas balloon for absorption or emission detection, as is presently done.

Water quality laboratories involved in arsenic monitoring should consider the differential pulse method. It is sensitive, quick, accurate, and does not require separation of arsenic prior to measurement. Laboratory evaluation of the method on water samples obtained in the field appears desirable.

Water quality laboratories should evaluate application of the flameless methods using a carbon rod, graphite furnace, or tantalum ribbon. Because flames are not used, there is no loss of arsenic lamp source intensity by absorption. Scattering losses caused by salts or particles in the furnace could be compensated by using a deuterium or hydrogen lamp, as is presently done in flame methods.

D. A[illegible]NOWLEDGMENT

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D.2. CONTENTS FOR CADMIUM-IN-WATER
MONITORING INSTRUMENTATION

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A. INTRODUCTION

Cadmium is one of the minor elements in terms of concentration in fresh and saline waters, but may be present in certain waste waters to a greater extent. It is one of the metals currently included in the EPA list of toxic pollutants.

Cadmium and cadmium compounds have a variety of beneficial uses. For example, the metal is used as a constituent of fusible alloys; a neutron shield in nuclear reactors; as a soft solder; in electroplating, as a corrosion protection overcoat for steel; and in nickel-cadmium storage batteries. Cadmium acetate is used to produce iridescent effects on porcelains and pottery; cadmium hydroxide is used in storage batteries; the yellow-colored cadmium sulfide finds application in coloring glass yellow, in phosphors and in solar energy cells; cadmium succinate has been used as a plant fungicide (Ref. 1, page 186; Ref. 2, page 884). In 1964, uses of cadmium as a metal represented 60-65% of the consumption of cadmium produced; approximately 55% was used for plating and 7% for alloys. The remainder of the cadmium produced was used for chemicals, particularly those in pigments and Ni-Cd batteries. The plating industry remains the largest user, consuming an estimated 2.2 x 10^6 kg (4.8 million lb) of the 5.4 x 10^6 kg (12 million lb) total consumed in the United States in 1972. This use was followed by the alloy, plastic stabilizer, television phosphor, and nickel-cadmium battery industries (Ref. 3).

Table A-1 shows selected physical properties of cadmium metal.

Additional information on cadmium and cadmium compounds may be obtained from The Merck Index (Ref. 1), The Encyclopedia of Chemical Technology (Ref. 2), and the Engineering and Mining Journal (Ref. 3).

1. Characteristics

Cadmium in water exists in the +2 oxidation state. The metal is soluble in mineral acids, but is insoluble in alkali hydroxides. Cadmium in water forms soluble complexes with ligands such as ammonia, cyanide, and halides. Soluble cadmium will react to form insoluble precipitates with anions such as carbonate, phosphate, oxalate, arsenate, sulfide, and alkaline hydroxides. Kopp and Kroner found that cadmium in surface waters of the United States exists primarily in the dissolved state, with none found in the suspended state (Ref. 4).

The natural background level of cadmium is quite low, justifying its inclusion among the minor elements. The cadmium content in drinking water has been reported to vary between 0.4 and 60 μg/l, with a mean of 8.2 μg/l. Cadmium salts may be found at above background levels in wastes from electroplating plants, pigment works, textile printing, lead mines, and chemical industries.

The daily intake of cadmium in man can vary from 4 to 60 μg, depending on the foods chosen. The major sources of cadmium in foods ingested by man appear to be seafoods and grains (Ref. 5, p. 149). At birth, the human body contains only 1 μg of cadmium; this increases to 30 mg at age 50 (Ref. 6). Toxic effects of cadmium in the human body are discussed in section 4.

Table A-1 Physical properties of cadmium (Ref. 2, page 885)

atomic number			48	
atomic weight (^{12}C = 12.000)			112.40	
melting point, °C			320.9	
boiling point, °C			765	
crystal system			hexagonal, close-packed	
lattice constant, Å			a = 2.9727; c = 5.606	
latent heat of fusion, cal/g			13.2	
latent heat of vaporization, cal/g			286.4	
coefficient of linear expansion, μin./(in.)(°C)			29.8	
capture cross section for thermal neutrons (2200 m/sec), b/atom			2450 ± 50	
electrical conductivity, percent of International Annealed Copper Standard (IACS)			25	
electrical resistivity, μΩ-cm ---	20°C		6.83	
	700°C		35.8	
specific heat, cal/(g)(°C) ---	20°C		0.055	
	321-700°C		0.06	
density, g/cm³ (temp, °C)	8.65(25)	$8.01(330_{liq})$	7.93(400)	7.56(700)
thermal conductivity cal/(sec)(cm²)(°C/cm)(temp °C)	0.22(20)	0.216(100)	0.105(360)	0.119(435)
vapor pressure, mm Hg (temp °C)	1(394)	10(484)	100(611)	400(711)
viscosity, cP (temp °C)	2.37(340)	2.16(400)	1.84(500)	1.54(600)

In 1970, Durum and Hem using atomic absorption analysis detected cadmium in 42% of the 727 samples taken of United States surface waters (Ref. 7). The concentrations ranged mostly from 1 to 5 µg/1. Samples of water were obtained in three locations: Public water supplies, U.S. Geological Survey hydrologic benchmark stations, and metropolitan-industrial complex locations. The implication of the data is that the higher concentrations of cadmium in water generally occur in areas of high population density. Cadmium was detected most frequently in the waters of New England and the northeastern United States, with a median concentration of 2 µg/1. See table A-2. Durum and Hem also found undissolved cadmium in bottom sediments of some of these waters.

2. Forms of Cadmium in Water

The forms of cadmium in water depend on the other constituents in the water, and on the pH. For example, in the presence of some ligands such as NH_3 or CH^-, cadmium forms complexes which are soluble in water above pH 6.7. In the absence of complexing ligands, Cd(II) ions are precipitated above pH 6.7. Cadmium ions react with dissolved carbonate, sulfides, phosphate, or aresnate to form insoluble precipitates and eventually bottom sediments.

Posselt and Weber published a report entitled "Environmental Chemistry of Cadmium in Aqueous Systems" (Ref. 8). The report includes models describing the equilibrium solubility of cadmium over a wide range of conditions in both natural and wastewaters.

3. Sources and Control of Cadmium in Water

The most common naturally occurring mineral is greenochite (CdS), which is found associated with zinc sulfide ores. The usual content in ZnS averages 0.3 to 0.4% CdS.

Background levels of dissolved cadmium in fresh waters are probably due to leaching and weathering of naturally occurring ores such as greenochite by rainwater. Wastewaters from electroplating plants, pigment works, chemical industries, and drainage water from lead mines can cause concentrations exceeding background levels. McKee and Wolf cite one study where ground-water contamination caused by wastes from electroplating industries reached 3.2 mg/1 of cadmium on Long Island, N.Y. In another case, high cadmium concentrations were reported in Missouri mine waters, where one spring contained 1000 mg/1 of cadmium (Ref. 5, page 149).

Cadmium can be removed from wastewaters in a number of ways. For example, added sodium sulfide will form the insoluble precipitate, CdS (Ref. 9), while cadmium in cyanide electroplating baths is precipitated by addition of a proprietary peroxygen formulation in the DuPont Kastone process (Ref. 10).

4. Toxic Effects

On being ingested, cadmium tends to concentrate in the liver, kidneys, pancreas, and thyroid of humans and animals. Once it enters the body, it is likely to remain. Normally, many plant and animal tissues contain about 1 mg of cadmium per kg of tissue, but there is no evidence that cadmium is biologically essential or beneficial.

> "Human beings have been sickened by 13 to 15 mg/kg of cadmium in popsicles, 67 mg/1 in punch, 300 mg/1 in a cold drink, and 530 mg/kg in gelatin. As little as 14.5 mg of cadmium taken orally has caused nausea and vomiting; yet in another instance, as much as 300 mg has not caused permanent injury. Four members of a family whose drinking water contained 0.047 mg/1 of cadmium had no history of adverse effects." (Ref. 5, p. 149).

Table A-2 Regional Summary of Cadmium in Surface Waters of the U.S. (from Ref. 7)

Region	Maximum (µg/1)	Minimum (µg/1)	Median (µg/1)	Not Detected (%)	Detected (%)
New England and Northeast	32	<1	2	36	64
Southeast	90	<1	<1	55	45
Central	40	<1	<1	55	45
Southwest	130	<1	<1	65	35
Northwest	21	<1	<1	78	22

Consumption of cadmium salts causes cramps, nausea, vomiting, and diarrhea. Oral ingestion of cadmium has been reported as the cause of a number of human deaths. A single dose of about 8.9 grams of cadmium chloride caused the death of a boy within 1.5 hours (Ref. 5).

The Itai-itai (ouch-ouch) disease which killed or disabled a number of residents along the Jinzu River in Japan was traced to cadmium discharges from a smelting plant (Ref. 11). The cadmium was ingested through consumption of farm products, fish, and water. There is no evidence to suggest that cadmium is accumulated in the bones of Itai-itai patients. Bones are dimineralized in advanced cases and become embrittled and weak largely due to loss of calcium (Ref. 30).

The acute lethal level of cadmium for fish varies from about 0.01 to about 10 mg/l, depending on diverse factors such as the test animal, the type of water, temperature, and time of exposure. Cadmium acts synergistically with other substances to increase toxicity to fish (Ref. 5).

Additional information on the toxic effects of cadmium are found in McKee and Wolf (Ref. 5), and in Water Quality Criteria, 1968 (Ref. 12).

5. Health Standards

The 1962 U.S. Public Health Drinking Water Standards list 10 μg/l cadmium as a cause for rejection of a water source. Water Quality Criteria, 1968, suggests a tolerance limit of 5 μg/l for irrigation waters used continuously on all soils, and 50 μg/l for short-term use on fine textured soils only (Ref. 12, p. 152). The EPA is expected to issue updated drinking water standards in the near future. Cadmium (and its compounds) is included on the EPA list of toxic pollutants. See Appendix B, H2O-Introduction, page 36.

B. INSTRUMENTAL METHODS

This section will survey primarily the literature on instrumental methods which are or might be applied to the monitoring of cadmium in water. Basically, methods discussed fall into one of the following two categories: (a) the standard methods now being used, (b) new techniques which might be more selective, more sensitive, or take less time than the standard methods. The literature covered will be selective; no attempt will be made to include all the publications on cadmium analytical methodology.

Standard Methods, 13th Ed., includes atomic absorption, molecular absorption, and polarographic methods for determining cadmium in waters (Ref. 13). Polarography is preferred to molecular absorption for wastewaters containing metals (Ref. 13, page 447). The U.S. Geological Survey Methods, Book 5 (Ref. 14) and the EPA Methods Manual (Ref. 15) both list atomic absorption methods.

1. Atomic Absorption

The primary limitation of atomic absorption as a means for analyzing fresh and saline water for cadmium is lack of sensitivity at the ambient Cd levels. For example, the U.S.G.S. Methods, Book 5, lists a direct method of aspirating the water sample into an air-acetylene flame using a Perkin-Elmer Model 303 . The optimum concentration range is given as 25 to 250 μg/l. The EPA Methods Manual (1971) gives 100 to 2000 μg/l as the optimum concentration range for direct aspiration using an Instrumentation Laboratories Model IL-153. In both cases an air-acetylene flame was used. Lower optimum concentration for direct aspiration is expected using newer atomic absorption instruments.

At very low levels of Cd, nonspecific absorption due to light scattering or molecular absorption may be a problem. This can be corrected using a H_2 or D_2 continuum lamp.

The analytical range is extended to cover 25 μg/l and less in the standard methods by chelating cadmium with ammonium pyrrolidine dithiocarbamate (APDC), followed by extraction into methyl isobutyl ketone (MIBK). None of the substances commonly occurring in natural water interferes with this method (Ref. 14). Instrumental parameters used by USGS, and readings obtained using a Perkin-Elmer Model 303 are shown in Table B-1.

Extraction of the cadmium-pyrrolidine dithiocarbamate chelate into methyl isobutyl ketone is carried out at pH 2.2 - 2.8, using 100 to 200 ml of the water sample contained in a volumetric flask, 2.5 ml. APDC (1.0 g/100 ml) solution is added, and mixed thoroughly with the water sample. At this point, the pH should be about 2.8. Ten ml of MIBK is added, and the flask then shaken vigorously for one or two min. Centrifugation may be required to achieve good separation between the MIBK layer and the water layer. The MIBK layer may then be decanted into another layer, and a second extraction made with MIBK. The MIBK layer containing the cadmium is then aspirated into the air-acetylene flame, and the reading obtained. See Table B-1 for readings obtained by USGS, together with the instrumental parameters used.

Table B-1 Perkin-Elmer Model 303 (from Ref. 14)

With this instrument the following operating conditions have been used:

Grating	Ultraviolet.
Wavelength counter	228.8 (2288A).
Slit	4.
Lamp current	6 ma.
Scale expansion	5×.
Source (hollow-cathode lamp)	Cd.
Response time control	1.
Burner	Boling.
Air pressure	28 psi; 6.0 on flowmeter.
Acetylene pressure	8 psi; 4.0 on flowmeter.

With these operating conditions the following readings have been observed:

Cadmium concentration (µg/l)	*Scale reading*
1.25	14.0
2.50	28.5
3.75	41.2
5.00	56.4

Solvent extraction of Cd with sodium diethyldithiocarbamate into methyl isobutyl ketone was used to analyze for Cd and Cu in Yamato River and Osaka Bay water samples (Ref. 16). The air-acetylene flame was used with a Perkin-Elmer Model 303 for the measurements. The extraction was carried out at pH 9 from a 500 ml filtered water sample into 20 ml of MIBK. The calibration curve for Cd was linear over the range 0.05 to 10 ppb (µg/l). Cadmium in the river water ranged between 0.07 to 0.82 µg/l, and 0.08 to 0.48 µg/l in the sea water.

An extraction method was used to analyze for Cd in plating wastes and river water (Ref. 31). Cadmium was extracted with 2-mercaptobenzothiazole into n-butyl acetate. The organic layer was then aspirated into an air-acetylene flame. The method permits the determination of cadmium over the concentration range 0.001 to 10.0 mg/l. Table B-2 shows the effects of cyanide and some metals which can be encountered in plating wastes.

The addition of a large amount of soluble zinc to a water sample permits almost total extraction of dissolved Cd by 2-mercaptobenzothiazole into butyl acetate (Ref. 17). Concentrations of cadmium as low as 0.02 µg/l can be determined, and the interference of cyanide is also overcome.

High-molecular weight amines such as tricaprylamine and N-dodecenyltrialkylmethylamine are excellent extractants for cadmium from iodide solutions (Ref. 18). Basically, the amines react with cadmium iodide to form a complex which is extracted into xylene, the organic phase. The preferred amine was tricaprylmethylammonium chloride, because it can be used for extraction from either alkaline or acidic solutions. The method may offer advantages over the presently used extraction techniques, and would seem to warrant investigation for application to water analysis.

Attention should be directed toward using clean glassware and chemicals of high purity so that the blank will be low. Any sample losses due to adsorption onto the walls of the laboratory glassware will cause low results. The standard additions method is suggested for determining percent recoveries.

The new flameless techniques certainly merit evaluation for cadmium in water because they are more sensitive than flame aspiration, and they are quicker than solvent extraction followed by flame atomization. For example,

Table B-2 Effect of Plating Waste Cations on Cadmium Determination (from Ref. 31)

Cd present mg/l	Foreign Ions Present mg/l						Cd found mg/l
	Cr(III)	Cu(II)	Ni(II)	Fe(III)	Zn(II)	$(CN)^-$	
10.0	0	0	0	0	0		10.0
10.0	5	5	5	5	5		10.1
10.0	10	10	10	10	10		9.77
1.00	0	0	0	0	0		1.00
1.00	5	5	5	5	5		0.92
1.00	10	10	10	10	10		0.88
0.100	0	0	0	0	0		0.100
0.100	5	5	5	5	5		0.112
0.100	10	10	10	10	10		0.067
2.0	0	0	0	0	0	100	2.3
2.0	0	0	50	0	0	100	2.7
2.0	0	0	75	0	0	100	2.4
2.0	0	0	100	0	0	100	2.5

the Varian AA6 atomic absorption instrument together with a Model 63 carbon rod analyzer was used to analyze cadmium in laboratory prepared water samples containing 10 µg/l Cd. Results obtained from this solution had a relative standard deviation of 1.6% for ten replicates. See Figure B-1. The greater inherent sensitivity of the carbon rod over that of the flame (130-fold) is also shown in Figure B-1 (Ref. 19). Using non-flame devices for determination of water samples, some suppression of the Cd signal was noted due to sulphates and chlorides. These are not serious, but do not occur in the flame (Ref. 30).

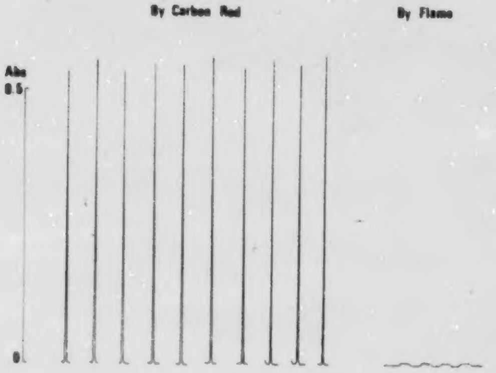

Figure B-1: 10 µg/l cadmium in laboratory prepared water sample: A. Ten replicates, using carbon rod excitation. B. Low signals obtained using flame excitation (Ref. 19).

The results achieved with a graphite furnace can vary widely with the voltage supplied to the device. The temperature of the graphite tube reaches 2700°C at 240 volts, but only 2500°C at 210 volts. The common U.S. voltage of 208 volts can be expected to produce still lower temperatures. This can be very significant when a refractory metal (e.g. Al) is being determined, and should be considered when a flameless instrument is chosen. High temperatures appear to be necessary in some cases to purge the graphite tube to avoid residual effects from the previous sample.

Matrix effects are also important in the use of the graphite furnace. Difficulty has been found in the determination of transition metals in sea water (Ref. 21), due primarily to sodium chloride and sodium sulfate. It was found possible to volatilize the major salts at lower than atomization temperatures, permitting the determination of Ni, Co, V, and Mn, but with such poor precision that the procedure is recommended only for monitoring large numbers of samples. Iron proved to be the only transition metal that could be determined in unpolluted sea water.

The residence time of the atomized metal in the optical path is basic in maximizing the signal. A comparison of the carbon rod vs. the carbon filament (Ref. 22) emphasizes this aspect of the method, and suggests a graphite tube configuration to achieve more of a closed system with attendant longer residence times.

A Perkin-Elmer Model 303 instrument equipped with a deterium background corrector and a Model HGA 70 graphite furnace was used to measure Fe, Ni, Cu, Co, Cr, Mo, Pb as well as Cd in dilute groundwaters and brines (Ref. 20). Argon was used as the purge gas. Sample aliquots were 10, 20, 50, or 100 µl. Careful injection of the sample aliquots was essential to obtain high precision: Each micropipet tip was rinsed three times with the water sample before injecting the sample, and was discarded after one use. Calibration of the instrument system was made using both a calibration curve and by the method of standard additions (the latter to take into account matrix effects). Reproducibility for Cd was rather poor, which the authors attribute to instability of the furnace power supply during atomization.

Generally, the authors found that detection limits were an order of magnitude better than those obtained using solvent extraction followed by flame atomization: 0.5 µg/l using the furnace vs. 5 µg/l using solvent extraction.

A later model of the Perkin-Elmer graphite furnace, the HGA-2000, offers increased convenience and thereby perhaps greater reliability. Flameless methods require extreme care in lamp alignment and other instrumental details to attain maximum sensitivity. This may account for unpublished reports of routine detection limits of 0.1 µg/l Cd for both the HGA-70 and HGA-2000 and sensitivity (with increasing error) to 0.002 µg/l Cd for the HGA 2000.

In summary, atomic absorption for cadmium utilizing solvent extraction followed by flame atomization appears to have the necessary sensitivity and specificity for water analysis. The flameless methods (carbon rod, graphite furnace, tantalum ribbon) should be evaluated because they appear to be more sensitive than the extraction-flame method, and may be quicker.

2. Emission Spectrometry

Cadmium is volatile, so that the sensitivity is considerably enhanced over that of less volatile metals. In many rocks and soils it is possible to detect and measure cadmium without chemical concentration (Ref. 23). The 228.8 nm line is most sensitive for Cd, but is not commonly used because it lies in the ultraviolet. Using the 326.1 nm line, the detection limit is only about 10 ppm, so that it is not sufficiently sensitive for direct measurement of cadmium in fresh or saline waters.

Emission spectroscopy using an induction-coupled argon plasma excitation source lowers the detection limit to 30 μg/l (228.8 nm Cd line) (Ref. 24), and 3 μg/l (326.1 nm line) (Ref. 25). The detection limit is thus comparable to that obtained by atomic absorption using an air-acetylene flame.

Conventional emission spectroscopy was used to measure cadmium (and other metals) in a comprehensive study (Ref. 4). Because of the low metal concentrations, water samples had to be pre-concentrated by evaporation prior to analysis.

Emission spectroscopy does not appear to have any advantages over the atomic absorption method for only cadmium analysis. If multi-element analyses are of interest, then the plasma excitation sources certainly seem to merit laboratory investigations for application to metals in water.

3. Molecular Absorption

Standard Methods, 13th Ed., lists the dithizone method for determining cadmium in fresh waters, and polluted waters. The minimum detectable concentration of 0.5 μg Cd, using a spectrophotometric cell with a 2-cm light path, while Cd in the water sample should fall in the range 1 to 10 μg for optimum results (Ref. 13, p. 77-80, p. 422-426).

Attention to the proper conditions for complexation, masking, and extraction is important to the successful application of the method, because dithizone nonselectively reacts with many metals. Selectivity for cadmium is achieved by extracting the Cd twice into a chloroform layer containing dithizone from 25-ml aqueous solution containing a mixture of sodium potassium tartrate solution, NaOH-KCN solution, $H_2NOH \cdot HCl$ solution, and the Cd being measured. The Cd reacts with dithizone to form a pink to red color, the intensity of the color depending on the amount of cadmium in the water sample. The Cd is extracted from the chloroform into a tartrate solution, and the chloroform layer is discarded. The Cd is then extracted back into a chloroform-dithizone solution from which the color intensity is measured with a spectrophotometer.

The method is tedious and time-consuming, but its reliability in terms of precision and accuracy have been established by analyzing synthetic unknown samples containing a mixture of 50 μg/l Cd, 500 μg/l Al, 110 μg/l Cr. 470 μg/l Cu, 300 μg/l Fe, 70 μg/l Pb, 120 μg/l Mn, 150 μg/l Ag, and 650 μg/l Zn. In 44 testing laboratories, the relative standard deviation was 24.6% with a relative error of 6.0% (Ref. 13, p. 80).

4. Polarographic Methods

Standard Methods, 13th Edition, includes a classical polarographic method with a dropping mercury cathode to analyze Cd in metal-bearing wastes and receiving streams (Ref. 13, p. 447). The method has the advantage of permitting simultaneous determination of Cd, Cu, Pb, Ni and Zn, but lacks sensitivity. Basically, the wastewater sample is wet-ashed with sulfuric and nitric acid, neutralized and filtered. The filtrate is then polarographically analyzed in three electrolytes: ammonium sulfate, ammonia-ammonium buffer, and finally the buffer containing added disodium ethylenediaminetetraacetate (EDTA). In effect, the EDTA eliminates the polarograms for Cd, Ni, and Zn.

Pulse polarography was applied to the measurement of Cd dissolved in a laboratory prepared solution (Ref. 25). The differential pulse method at a stationary mercury electrode gave a well-defined signal for a concentration of Cd as small as 4 μg/l (4×10^{-8} M) in a solution of 0.015 M KH_2PO_4, pH ≈ 4.6. See Figure B-2. Extraction of the Cd was unnecessary; measurement was made directly at this concentration level.

Anonic stripping voltammetry has been applied to Cd analysis in both fresh and wastewaters (Ref. 26, p. 248). Samples were digested before analysis to measure total metals or filtered to measure dissolved metals in the filtrate and, after digesting, in the particulates. Cadmium was measured over the range 0.3 to 7.4 μg/l.

In summary, classical polarographic methods have been applied to Cd in water. The differential pulse method which can measure Cd at 4 μg/l in laboratory prepared solutions should be evaluated for application to water samples. The detection limit appears comparable to that of atomic absorption using extraction, and the multielement possibility is attractive.

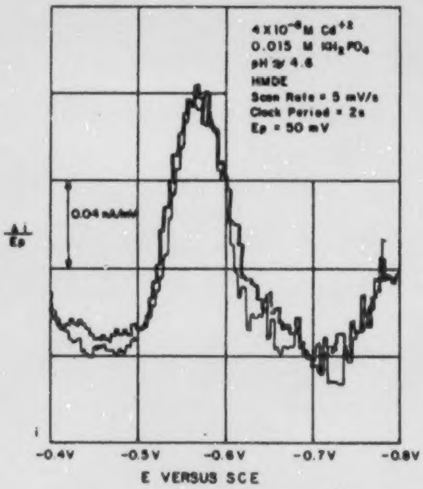

Figure B-2: Differential PP for Cd(II) (2 repetitions) 4 × 10^{-8} M in 9.075 KH_2PO_4 at a hanging mercury drop electrode. (Ref. 25).

5. Other

a. Neutron Activation Analysis

Application of neutron activation analysis to water samples was reviewed recently (Ref. 27). Reported sensitivity for cadmium in pure water was 0.1 ppm (mg/l) and only 40 ppm (mg/l) in tap water. The samples were irradiated in a thermal flux of 1.8×10^{12} N $cm^{-2}sec^{-1}$ for 30 min prior to measurements with a 3" x 3" NaI(Tl) detector.

A report was published on the technology and application of neutron activation analysis for the measurement of trace metal constituents including Cd in fresh water, sea water, marine organisms, sediments, and atmospheric particulates (Ref. 28).

b. X-Ray Fluorescence

Cd and some other metals (Fe, Mn, Zn, Cu, As, Pb, Se) were measured in water at concentrations as low as a few ppm (mg/l). The metals were precipitated from the water with a carrier of the metals by either diethyldithiocarbamate or 1-(2-pyridylazo)-2-naphthol, and filtered. The precipitate collected on the filter was then analyzed for the metals content (Ref. 29).

C. SUMMARY AND CONCLUSIONS

Presently used standard methods to monitor cadmium in water are principally either atomic absorption or molecular absorption. The atomic absorption method usually requires extraction of cadmium as the ammonium dithiocarbamate complex into methyl isobutyl ketone solvent, followed by aspiration into an air-acetylene flame. Direct aspiration is possible, if the Cd concentration falls in the range about 25 to 250 µg/l. The molecular absorption method using dithizone is neither specific nor sensitive for measuring Cd in fresh water, but is made both sensitive and selective by extraction methods.

The main difficulties associated with the monitoring of Cd in water are lack of sensitivity and selectivity of the presently used methods. Both of these difficulties would appear resolvable through application of flameless atomic absorption methods (e.g., the carbon rod analyzer) differential pulse polarography, or anodic stripping to analysis of field samples.

D. ACKNOWLEDGMENT

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D.3. CONTENTS

FOR

LEAD-IN-WATER MONITORING INSTRUMENTATION

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A. INTRODUCTION

Lead is easily extracted from its ores which no doubt accounts for its use from earliest times. The earliest known specimen is a lead statue dating from before 3800 BC found at the Dardanelles on the site of an ancient city called Abydos. The metal is mentioned in Exodus and other sections of the Old Testament. Lead was used extensively to manufacture water pipes; the Romans produced pipes in standard diameters and regular 10-foot lengths. It is estimated that the Roman Empire extracted and used six to eight million tons of lead over a period of 400 years.

In modern times lead and its compounds have a number of beneficial uses. For example, the metal is used as a lining material in the manufacture of sulfuric acid; in petroleum refining; for x-ray and atomic radiation protection; in gasoline additive, tetraethyllead; in storage batteries; in solder alloys; and in paint pigments. Lead acetate is used to detect sulfide and as a topical astringent; lead arsenate is a constituent of various insecticides for larvae of gypsy moth and boll weevil; lead carbonate and lead chromate, as pigments; lead sodium thiosulfate, in matches; and lead sulfide, to glaze earthenware. In 1968, the United States mined 374.1 thousand short tons of lead, and refined 913.4 thousand short tons. The estimated totals in 1972 were 643.7 thousand and 1,209.2 thousand short tons, respectively. The United States consumed a total of 1,355,800 short tons of lead in 1972, compared with 1,209,300 in 1968.

Table A-1 shows physical and chemical constants of lead.

TABLE A-1

Physical and Chemical Constants of Lead
(from Ref. 2, p. 207)

atomic number	82
atomic weight	207.19
crystal system	face-centered cubic
melting point, °C	327.43
boiling point, °C	1740
sp gr, at 20°C	11.3437
at 327.43°C	10.686
at 650.0°C	10.302
at 850.0°C	10.078
vapor pressure, at 987°C, mm Hg	1.0
at 1167°C	10.0
at 1417°C	100.0
at 1508°C	200.0
at 1611°C	400.0
surface tension, at 350°C, dyn/cm^2	442
at 400°C	438
at 500°C	431
viscosity, at 441°C, cP	2.116
at 551°C	1.700
at 703°C	1.349
at 844°C	1.185
sp heat, at 0°C, cal/g	0.0297
at 20°C	0.0306
at 100°C	0.0320
at 327°C	0.0390
at 500°C	0.037
latent heat of fusion, cal/g	5.86
latent heat of vaporization, cal/g	203
thermal conductivity, at 20°C, cal/(cm^2) (°C/cm)(sec)	0.083
at 100°C	27.021
at 327.43°C	94.6
at 600°C	107.2
at 800°C	116.4
electrolytic soln potential (hydrogen = 0), V	0.122
magnetic susceptibility, 10^{-6} cgs units	0.12
Brinell hardness (cast)	4.2

Additional information on lead and lead compounds may be obtained from The Merck Index (Ref. 1), The Encyclopedia of Chemical Technology (Ref. 2), and the Engineering and Mining Journal (Ref. 3).

1. Characteristics

The predominant form of lead in water is the +2 oxidation state. The metal is soluble in hot concentrated nitric acid, and in acetic acid. Lead forms soluble complexes with salts such as the acetate and chloride, but the carbonate and hydroxide are insoluble and the sulfide is only slightly soluble. Fresh and treated waters seldom contain more than 20 μg/l of lead; higher levels may occur near industrial, mine and smelter discharges, or from old plumbing. Because of the insolubility of the carbonate and hydroxide, and the sparingly solubility of the sulfate, lead will not remain long in the soluble form in fresh waters.

The mean daily intake of lead by adults in North America from all sources is about 330 μg. Of this amount, 10 to 30 μg is ingested from water used for cooking and drinking. The remainder is derived from air, tobacco smoke, beverages, and foods. Toxic effects of lead are discussed in Section 4.

In 1970 Durum and Hem using atomic absorption analysis detected lead in 63% of the 727 samples taken of United States surface waters (Ref. 4). The concentrations ranged primarily from 1 to 50 μg/l and was most frequently 1-5 μg/l. Samples of water were obtained in three locations: public water supplies, U.S. Geological Survey hydrologic benchmark stations, and metropolitan-industrial locations. Lead was detected less frequently in samples collected at benchmark sites than in those from public water supply sources and from streams below metropolitan-industrial areas. Lead had a distinct regional pattern. It occurred most frequently in the well-watered northeast and southeast and coincides with similar patterns in rainfall found by others who found that the highest rates of lead fallout occurred in the northeast, southeast, and eastern part of the central regions of the United States. See Table A-2.

Table A-2

Regional Summary of Lead in Surface Waters of the U.S.
(from Ref. 4)

	Concentration, μg/l			Not Detected	Detected
Region	Maximum	Minimum	Median	%	%
New England and Northeast	890	1	6	8	92
Southeast	44	1	4	27	73
Central	84	1	1	51	49
Southwest	34	1	1	61	39
Northwest	23	1	1	62	38

2. Forms of Lead-in-Water

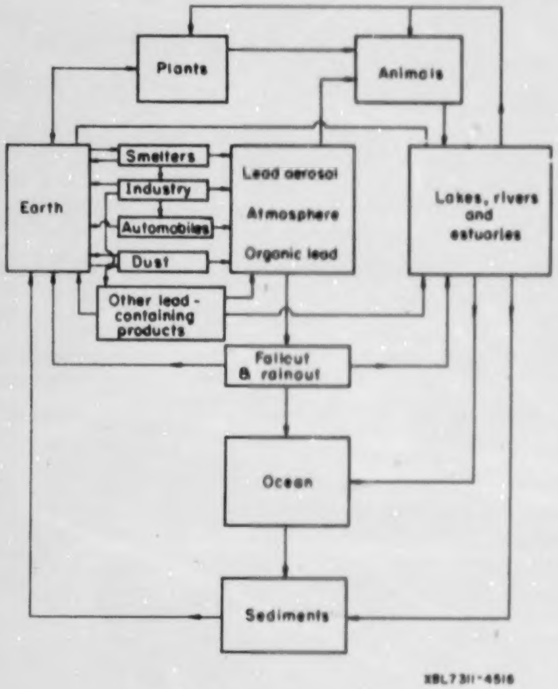
The forms of lead-in-water depend on the other constituents in the water, the temperature, and on the pH. For example, lead chloride ($PbCl_2$) is soluble in 93 parts of cold water but only 30 parts of boiling water. Lead chloride is also readily soluble in solutions containing an excess of chloride ions such as ammonium chloride. On the other hand lead ions react with dissolved carbonate, sulfide, arsenate, chromate, sulfate, phosphate, or hydroxide to form insoluble precipitates and eventually bottom sediments in water streams.

Additional information on the forms of lead-in-water may be obtained from Water Quality Criteria (Ref. 5, page 206).

The pathways by which lead enters the environment from its origin on the earth are poorly characterized. Figure A-1 gives an ecologic flow chart of the major compartments and pathways of lead transformation in the biosphere. There has been no comprehensive study of its translocation within living systems. There is not sufficient information on the chemical forms, amounts, and rates of transfer of lead from one compartment of the environment to another to permit treatment of the subject in terms of systems analysis. However, fragmentary data affords some insight into the movement of lead in the biosphere. These data come primarily from studies of lead-210, a radionuclide important in tracing the pathways and determining flux rates of lead, as stressed by Burton and Steward (Ref. 6).

Figure A-1:

Ecologic Flow Chart for Lead Showing Possible Cycling Pathways and Compartments



3. Sources and Control of Lead-in-Water

Lead in the earth occurs chiefly as the mineral galena (PbS), and also as carbonate in cerussite and as a sulfate in anglesite. Lead occurs in the earth's crust to the extent of about 15 g/ton or about 0.002%. Background levels of dissolved lead in fresh waters are probably due to leaching and weathering of the naturally occurring minerals. Wastewaters from various industrial and mining effluents, the dissolving action of water on lead pipes (plumbosolvency), and lead from automobile emissions may result in levels of lead-in-water above that of the natural background levels. See Fig. A-1. The characteristics of water, soft or hard, that appear to be conducive to plumbosolvency include comparative absence of calcium and magnesium bicarbonates, low pH, high dissolved oxygen, and high nitrate content (Ref. 5). See H20-MET, Introduction, page 3, for Table A-4 which shows the heavy industries with which lead discharge is associated.

Lead can be removed from wastewaters in a number of ways; for example, lime treatment followed by soda ash (Ref. 7).

4. Toxic Effects

On being ingested, lead tends to be deposited in bone as a cumulative poison. Typical symptoms of advanced lead poisoning are constipation, loss of appetite, anemia, abdominal pain, and tenderness, pain and gradual paralysis in the muscles, especially in the arms. A milder and often undiagnosed form of lead poisoning also occurs in which the only symptoms may be lethargy, moroseness, constipation, flatulence, and occasional abdominal pain. Lead poisoning usually results from the cumulative toxic effects of lead after continuous consumption over a long period of time, rather than from occasional small doses. Immunity to lead cannot be acquired, but sensitivity to lead seems to increase. Lead is not among the metals considered essential to the nutrition of animals or human beings. Low levels of lead poisoning in rats produced changes in normal metabolism, of brain norepinephrine accompanied by abnormal behavior such as hyperactivity and aggressiveness. Low levels of chronic lead intake by the rats from birth to adulthood led to increases in brain lead content and increases in norepinephrine turnover (Ref. 5, 8).

On the other hand, lead intake produced no ill effects on laboratory mice and seemed to negate the toxic effects of methyl mercury. Lead given as lead diacetate, $Pb(OAc)_2$, at either 5,000 or 10,000 mg/l in drinking water caused no observable effects and was not lethal in 80 or 52 days, respectively. Methyl mercury, as CH_3HgOH, had no observable effects in drinking water at 5 mg/l but produced rapid weight loss and death within 20 to 33 days at the 25 mg/l level. The combination of 5,000 mg/l lead and 25 mg/l methyl-mercury, however, produced no consistent growth or behavioral effects and only one mouse in six died in 80 days (Ref. 9).

Lead may enter the body through food, air, and tobacco smoke, as well as from water and other beverages. Consequently, the total intake of lead must be considered in setting standards for water. The maximum acceptable load of Pb from food and beverages has been tentatively placed at 0.005 mg per kg per day (Ref. 10). Lead in an amount of 0.1 mg ingested daily over a period of years has been reported to cause lead poisoning. The daily ingestion of 0.2 mg lead is considered excessive by one authority. On the other hand, one reference considered 0.5 mg/day safe for human beings and a daily dose of 2.0 mg for a one-year period apparently did not affect the health of one adult (Ref. 5, p. 206). An excellent discussion on the effects of traces of lead in industrial water supplies, irrigation water, water to be used for watering stock and wildlife, and fish and other aquatic life, is given in Water Quality Criteria, by McKee and Wolf (Ref. 5).

5. Health Standards

The 1962 U. S. Public Health Drinking Water Standards and the 1975 Interim Drinking Water Standards list 50 μg/l as constituting grounds for rejection of the water supply as unsuitable for use in drinking. The third edition of the International Standards for Drinking-water lists a tentative level of 100 μg/l of lead in water which is used for drinking purposes and the maximum acceptable load of lead from food and beverages has been tentatively placed at 5 μg/kg/day (Ref. 10).

B. INSTRUMENTAL METHODS

This section will survey primarily the literature on instrumental methods which are, or might be, applied to monitoring the lead content of water. Basically, methods discussed fall into one of the following categories: (a) the standard method, now being used; for example, that listed in Standard Methods, 13th edition; and (b) new techniques which might be more selective, more sensitive, or take less time than the standard methods. The literature covered will be selective; no attempt will be made to include all the publications on lead analytical methodology.

Standard Methods, 13th edition, includes atomic absorption, molecular absorption, and polarographic methods for determining lead in waters. Polarography and molecular absorption are listed for methods for analyzing lead-in-wastewaters (Ref. 11). The United States Geological Survey Methods, Book 5 (Ref. 12), the EPA Methods Manual (Ref. 13), and ASTM, Part 23 (Ref. 14) list atomic absorption methods.

1. Atomic Absorption

The primary limitation of flame atomic absorption as a means of analyzing fresh, waste, and saline water for lead is lack of sensitivity at levels required for ambient lead determination. The detection limit is dependent in large measure on the type of instrumentation employed in flame atomic absorption spectrophotometry. The type of burner, length of flame path, the gaseous fuel used, the oxidant used, the flame temperature, and the degree of expansion of the meter or other recorder, all influence the lowest concentration that can be detected by flame atomic absorption. A direct method involving aspirating the water sample into an air-acetylene flame is given in the ASTM Book and the EPA Manual. The concentration range for the direct method of analyzing lead is listed as 0.34-40 mg/l in the ASTM method and 1-10 mg/l using the EPA method. The analysis of lead is exceptionally sensitive to turbulence and absorption bands in the flame, using the air-acetylene flame. Therefore care should be taken to position the light beam in the most stable central portion of the flame. The direct EPA method suggests using the 217.0 nm line of lead and indicates that a sensitivity of 60 μg/l and a detection limit of 10 μg/l are achievable. In the ASTM method the 283.3 nm lead line is used for the analysis. The unknown water samples must be analyzed under exactly the same conditions as those used in establishing the calibration curve.

For lead concentrations below about 0.2 mg/l an extraction procedure involving chelation of lead with ammonium pyrrolidinedithiocarbamate is used. For example, in Standard Methods, 13th edition, p. 213, the water sample is adjusted to pH 2.2-2.8 by adding hydrochloric acid. Ammonium pyrrolidinedithiocarbamate solution and methylisobutylketone are added, and the Pb chelate extracted from the water sample by shaking. The extraction is repeated with a second portion of methylisobutylketone (MIBK) and the two extracts combined. The metal in the methylisobutylketone as well as the standards are determined using the 283.3 nm wavelength and an air-acetylene mixture. For organic solvents such as MIBK, the fuel-to-air ratio must be reduced because the burning of the MIBK organic solvent contributes to the acetylene fuel supply and this is observed in two ways: it may lift the flame off the burner, or it may introduce an undesirable luminescent black background to the flame. Standard Methods, 13th edition, also recommends setting the fuel-to-air ratio of the gas mixture at the burner by starting with the settings recommended by the manufacturer for the analysis of lead and then gradually reducing the acetylene flow while the solvent is being aspirated until the flame is similar to the flame that is obtained for aspiration of the MIBK organic solvent. In the case of air-acetylene,produce as blue rather than as white a flame as possible. Adjust the acetylene flow of the nitrous oxide burner until the flame is rose-red, approximately double that for an air-acetylene burner.

Solvent extraction techniques applied to lead analysis in water samples have proved to be useful in concentrating the metal as well as removing the metal from interfering matrices. However, one drawback is the instability in storage of some of the metal chelates in the solvent used for extraction. The instability manifests itself as a fine precipitate in MIBK solvent with a subsequent loss in signal and consequent clogging of the burner. One approach to this problem of storing samples of metals that have been extracted into MIBK is that used in the following for lead, manganese, and cadmium. The lead was chelated with a 5% solution of diethyldithiocarbamate at pH 3.5 and then extracted into MIBK. After 15 minutes, the MIBK layer was drawn off into glass-stoppered volumetric flasks. Approximately 40 ml of MIBK are recovered after separation from the aqueous phase. Thirty-five ml of each MIBK extraction solution were pipetted into 500 ml evaporation flasks and evaporated to dryness under partial vacuum at 50°C. After the evaporation flasks had cooled to room temperature, 35 ml of a mixture of one part acetone plus one part 0.1 N HCl were added to each flask and swirled until the metal chelate residue dissolved. This required about one-half minute. The acetone-HCl solutions were transferred quickly to 60 ml polycarbonate bottles. The extracted metal solution could then either be immediately aspirated from the bottles into the flame or aspirated into the flames after two weeks' storage (Ref. 15).

Besides ammonium pyrrolidine dithiocarbamate and diethyldithiocarbamate, dithizone, oxine, and a dithizone-oxine-acetylacetone combination have also been used to extract lead. Procedures using chelating resins have been described (Ref. 16). Other specialized atomization procedures may be used to increase lead detection limits. For example, the Sampling Boat and Delves Cup methods have detection limits to 1 μg/l using one ml and 0.1 ml sample volumes respectively. The graphite furnace is capable of detecting as low as 0.05 μg/l of lead. It has been used for freshwater analysis by several workers (Ref. 16).

A Perkin-Elmer Model 303 instrument equipped with a Model 56 recorder, a deuterium background corrector, and a Model HGA-2000 heated graphite atomizer with continuously varying time and temperature selection for sequentially drying, charring, and atomizing the samples was used to evaluate application of a heated graphite atomizer for the routine determination of lead and other metals in water. Graphite tubes 5.3 cm long and 1 cm in diameter were used. The tube interior was purged with argon to prevent combustion of the tube and to inhibit oxidation of the atomized elements. Eppendorf microliter pipettes with disposable plastic tips were used to introduce the solutions of the metals into the interior of the graphite tubes through a central hole in the tube wall.

Water is evaporated at low temperatures and the sample then ashed or charred at a higher temperature, and finally, atomized at a still higher temperature. See Table B-1 for the drying, charring, and atomization temperatures and times. The method was evaluated by distributing standard reference water samples containing Pb and other elements to cooperating laboratories. The mean concentration and standard deviation of each constituent and the number of participating laboratories are given in Table B-2 (Ref. 17).

TABLE B-1

Operating Conditions of Perkin-Elmer Model 303 AAS & HGA-2000 (from Ref. 17)

	Cu	Pb	Cd	Mn	Cr
Wavelength, nm	324.7	283.3	228.8	279.5	359.4
Special band width, nm	0.7	0.7	0.7	0.7	0.2
Drying temperature, °C.	110	110	110	100	100
Drying time, sec.	40	40	40	40	40
Charring temperature, °C.	1000	550	400	1100	1350
Charring time, sec.	90	90	90	90	90
Atomizing temperature, °C.	2500	2000	1500	2400	2700
Atomizing time, sec.	20	20	25	20	20

TABLE B-2

Standard Reference Water Samples
(from Ref. 17)

Constituent	Mean concentration ± standard deviation, μg/l (No. of laboratories) (Most determinations by conventional flame atomic absorption)			
	SRWS No. 25	SRWS No. 28	SRWS No. 32	SRWS No. 38
Acidity	26000±900(24)			
Al	540±60(18)	610±70(31)	243±72(60)	400±52(20)
As	38±18(12)	54±16(13)	58.1±15.6(15)	9.8±4.1(13)
Be				27±5(6)
Cd		11.9±4.7(23)	9.9±2.2(41)	3.6±1.1(21)
Cr		19.2±14.3(32)	11±11(37)	45±24(20)
Cu	119±30(23)	240±32(49)	591±59(54)	145±38(29)
Fe	397±19(29)	115±32(57)	831±97(60)	1008±106(31)
Pb		70.0±18.7(32)	27.2±12.0(39)	16.7±9.0(21)
Li	484±25(20)			
Mn	300±49(24)	66±17(54)	110±17(56)	35±13(27)
Hg			6.19±2.25(22)	3.32±0.86(14)
Ni		6.8±6.5(16)	23.2±5.2(14)	
pH	1.79±0.17units(28)			
Ag		41.2±38.7(6)		
Sr	279±28(21)	75±29(19(		
Zn	112±28(22)	22 ±34(46)	549±29(52)	192±29(29)
	Concentration, mg/l			
Ca	24	8	26	18
Mg	8.5	1.5	9.7	6.2
Na	20	5.7	24	14
SO_4	32	18	48	28

Constituent	Mean concentration ± standard deviation, μg/l (No. of determinations by emission spectroscopy by one laboratory)			
	SRWS No. 25	SRWS No. 28	SRWS No. 32	SRWS No. 38
Al	555±48(59)	623±48(22)	215±25(27)	401±35(15)
Ba	38.5±3.6(51)	580±53(21)	51.8±5.0(26)	28.3±1.8(15)
B	351±73(30)	5.5±0.8(24)	15.8±2.0(24)	9.8±1.6(15)
Cr	13.6±0.8(45)	22.2±1.8(25)	10.0±1.1(23)	53.0±5.2(14)
Cu	79±9.6(52)	273±32(24)	620±67(25)	126±13(15)
Fe	392±29(28)	142±11(25)	900±40(24)	1200±97(13)
Pb	14.9±2.1(60)		26.9±2.8(25)	16.2±1.8(15)
Mn	313±29(26)	77±8(25)	129±18(25)	41.5±7.7(14)
Mo	88±17.7(29)	3.2±0.4(21	18.2±1.3(18)	9.4±1.0(10)
Ni	15.6±3.0(48)	4.9±0.8(25)	30.4±3.8(27)	4.4±1.3(15)
Ag	4.9±1.4(42)			
Sr	250±32(61)	582±53(22)	255±26(21)	156±13(13)
V			4.6±0.7(20)	7.6±0.9(10)
Zn			592±72(20)	187±15(10)

The number of useful atomizations obtainable from the graphite tubes used in this study was found to be significantly less than the 50-300 quoted by the manufacturer, Perkin-Elmer. While many factors influence the number of useful atomizations, including atomization temperature, salt content of samples, and duration of interruption of gas flow during the initial few seconds of atomization to enhance sensitivity, no tubes in practice gave satisfactory reproducibility of absorption signals up to 50 atomizations. Typically, though not invariably, poor reproducibility became evident after 25 or 30 atomizations when using 8-second gas flow interruptions. Wiping both the interior and exterior of a used tube with tissue paper in some cases permitted a few additional useful atomizations. However, in general, tubes were discarded and replaced as soon as poor reproducibility became evident. The need to check continually for reproducibility itself lessened the number of other atomizations obtainable on an individual tube. The authors note that if some degree of sensitivity can be sacrificed, it is often possible the life of a tube can be extended by not interrupting the gas flow during atomization. Installation of a new tube, currently $3.00 each, took about three minutes. An attempt to use grooved graphite tubes was discontinued when it was observed that they do not reach the same maximum temperature as do the standard tubes because of a difference in electrical resistance. A calibration curve showed a cut-off maximum temperature slightly over 2200°C obtainable with these tubes on the HGA 2000 atomizer. This upper temperature limit would preclude atomization of 26 of the 41 elements listed at the temperatures recommended by the manufacturer's brochure. However, satisfactory results could be obtained at lower temperature though with loss of sensitivity. Perkin-Elmer notes that the shorter lifetime of the graphite electrodes used in this study could be traceable to the gas interrupt feature which is used constantly with maximum temperature (Ref. 17).

The sensitivity found here for lead is the same order of magnitude as that reported by Perkin Elmer. See Table B-3. The following interferences for lead were noted on the absorption signal produced by a standard containing 100 µg/l Pb. Sodium sulfate suppressed the absorption signal at 50 mg/l sulfate but was not tested at lower concentrations. NaCl at 10 mg/l Na$^+$ suppressed it to 25% of the original signal; MgCl$_2$ at 500 mg/l Mg^{++} suppressed it to 33%; calcium chloride at 5000 mg/l Ca^{++} caused an erratic signal. Earlier, it had been found that the Pb absorption signal is reduced with increasing amounts of NaHCO$_3$. It was also noted that there was a matrix effect when determining Pb in river water and it was recommended that the method of standard additions be used to compensate for interferences caused by matrix effects.

TABLE B-3

Comparison of Sensitivities Obtained in This Study and as Listed by Perkin-Elmer (from Ref. 17)

Element	+Sensitivity(picograms/1% absorption)	
	This Study	Perkin-Elmer
Cd	2.4	0.2
Cr*	34	25
Cu	36	50
Pb	20	50
Mn	7.2	8

*In this study the 359.35 nm wavelength, rather than the 357.87nm wavelength recommended by Perkin-Elmer, was used.

+Sensitivity is the weight of the element which gives 1% absorption.

Results obtained here were similar to those also obtained by analyzing the standard reference water samples on a Varian Techtron Model AA5 instrument and Model 63 carbon rod atomizer which, although significantly different in design from the Perkin-Elmer heated graphite atomizer, produced very comparable results. Many of the interferences observed earlier with the heated graphite atomizer were tested and confirmed with the carbon rod atomizer. The authors concluded that although the heated graphite atomizer has high capabilities of sensitivity and detection limits for many elements, it may have potential applications for specific problems encountered in water analysis; its usefulness for routine practical analysis of water of varied compositions, especially by laboratories engaged in the analysis of large numbers of samples, is limited.

In summary, atomic absorption for lead utilizing solvent extraction followed by flame atomization has the necessary sensitivity and specificity for most water analyses. The flameless methods should be evaluated for any advantages such as higher sensitivity or more rapid analysis of lead than current methods.

2. Emission Spectrometry

Flame, arc, spark, and plasma excitation emission spectrometry are discussed in H20-MET, Instrumentation, page 2, Section 1.

A conventional direct-reading emission spectrograph was used to measure lead and other metals in a comprehensive study of trace metals in waters of the United States (Ref. 18). Because of the low metal concentrations, water samples had to be preconcentrated by evaporation prior to analysis. For lead the detection limit was 40 μg/1 in water samples having a total dissolved solid content of 400 mg/1. The term "detection limit" is used to indicate the lowest concentration of lead that can be distinguished from background noise or interference. The lower detection limit for lead and other metals in water may be extended to less than 10 μg/1 by using the new plasma excitation emission spectroscopy.

A spectrochemical method for the determination of lead and 35 other elements in industrial effluent was recently reported (Ref. 19). A 2M Applied Research Laboratory (ARL) Spectrograph with both 24,000 and 36,000 lines/in. gratings and the ARL Multisource Model No. 5700 was employed. A Jarrell-Ash Recording Microphotometer Model 23-100 was used to obtain photometric measurements for computer calculations. The 70% argon-30% oxygen atmosphere was obtained with a Stallwood jet. For mechanical grinding and blending operations, Spex Mixer/Mills No. 5000 and No. 8000 were used.

Samples were taken from primary plant waste streams around the Newark, New Jersey, facilities of Englehard Minerals and Chemicals Corporation. The preliminary data obtained on these samples showed a predominant chloride system containing minor amounts of nitrates and sulfates in addition to their free-acid counterparts. Although most of the basic streams were ammoniacal, some solutions containing free sodium hydroxide were also encountered. Sodium and calcium were found to be the only persistent matrix elements and these were at various concentrations. From this information, original synthetic matrices were selected for the standards and were composed of sodium chloride as the major, and calcium chloride as the minor, constituent. During the investigation, it was observed that calcium did not exert any particular influence on the impurity elements and was, subsequently, eliminated in the standard preparation. The standards were prepared by dissolving sodium and/or calcium chloride salts containing 200-300 mg sodium per 100 ml and 50 mg of calcium per 100 ml in a 100-ml volumetric flask. When NaCl was used as a single matrix salt, 250-300 mg of Na per 100 ml is used. A total of 11 series of standards was prepared for this investigation. Nine series were prepared as a chloride system, one as a nitrate system for silver, and one as a magnesium-calcium matrix for the determination of sodium. See Table B-4 for a comparison of the spectrographic method and atomic absorption data on synthetic effluent HR-400.

TABLE B-4
Accuracy of Method: Comparative Spectrographic and AAS Data on Synthetic Effluent HR-400
(from Ref. 19)

Elements	Concentrations Added, mg/1	Spectrographic Method, mg/1	AAS Method, mg/1
Na	1000	984	--
K	25	26	24.82
Ca	20	22	19.6
Fe	5	5.4	4.9
Zn	5	4.0	5.77
Ru	5	5.2	5.1
Ir	5	5.2	4.0
Mg	1	1.0	0.96
Cu	1	0.92	1.04
Ni	1	0.87	1.0
Pb	1	1.1	1.0
Ti	1	1.0	1.0
Mn	1	1.0	1.0
Pt	1	1.1	1.0
Cd	0.5	0.42	0.47
Pd	0.1	0.11	0.1
Rh	0.1	0.14	0.1
Au	0.1	0.12	0.1
Cr	1.0	0.98	--
Mo	1.0	1.1	--
Be	0.5	0.51	--

In conclusion, emission spectroscopy does not appear to have any advantages over the atomic absorption method if only lead is being determined. If multi-element analyses are of interest, then the plasma excitation sources certainly merit laboratory investigations for application to metals in water.

3. UV-VIS (Colorimetric)

Standard Methods, 13th edition, lists the dithizone method for determining lead in fresh waters and as a tentative method for analyzing lead in polluted waters. For fresh waters the minimum detectable concentration is approximately 2 μg of lead, while lead in the water sample should be around 15 μg per 25 ml of sample for optimum results (Ref. 11, p. 196 and p. 436).

Attention to the proper conditions for complexation, masking,and extraction is extremely important to the successful application of the method because dithizone nonselectively reacts with many metals. The procedure is extremely sensitive for lead, and measurable amounts of lead may be picked up from glassware and reagents. Samples should be collected in bottles made of lead-free glass or plastic containers. If possible, separatory funnels used in lead determination should be reserved for this purpose only. Interferences by most metals which form dithizonate are eliminated by double extraction at controlled pH. In the first extraction ammonium citrate and cyanide will complex many potentially interfering heavy metals. Hydroxylamine inhibits dithizone oxidation by ferricyanide which is produced by any iron present in the water sample. Tin in large amounts can be removed prior to analysis for lead by volatilization or, less satisfactorily, by ignition. The analysis should be carried out in diffuse light since bright sunlight tends to oxidize dithizone to dithizonate. The elements that interfere with the extraction of lead in cyanide medium at pH 8 to 9 are bismuth, stannous tin, and thallium. However, thallium is seldom encountered in the usual water samples. On the other hand, bismuth and, in particular, tin occur quite frequently; hence, special attention must be given to their separation prior to analysis. For wastewater samples, hydrazine acetate solution is used instead of the hydroxylamine hydrochloride.

For wastewater samples the sample is pretreated by nitric-acid perchloric acid digestion. See p. 418, Ref. 11. Selectivity for lead is achieved by extracting the lead into a CCl_4-dithizone solution from 25 ml aqueous solutions containing a mixture of ammonium citrate reagent, ammonium hydroxide, and potassium cyanide solution at pH 8.5-9. The CCl_4 layer will be red due to the formation of a lead dithizonate compound. The lead is extracted into a dilute nitric acid solution by shaking an aqueous solution of nitric acid with the CCl_4 layer containing the lead dithizonate. This is followed by extracting the lead back into the CCl_4 solution of dithizone after adding ammonium citrate reagent to the dilute nitric acid extract.

The method is tedious and time-consuming, and the atomic absorption method which entails fewer operations on the sample is preferable. The accuracy and precision have been established by analyzing synthetic unknown samples containing a mixture of 70 μg/l Pb, 500 μg/l Al, 50 μg/l Cd, 110 μg/l Cr, 470 μg/l Cu, 300 μg/l Fe, 120 μg/l Mn, 150 μg/l Ag, and 650 μg/l Zn in distilled water. The relative standard deviation was 42.1% with a relative error of 8.5% when tested by 43 laboratories (Ref. 11, p. 199).

4. Polarographic Methods

Standard Methods includes a classical polarographic method with a dropping mercury electrode to analyze lead in metal-bearing wastes and receiving streams (Ref. 11, p. 447) The method has the advantage of permitting simultaneous determination of cadmium, copper, nickel, and zinc as well as lead, but lacks sensitivity. Basically, the waste water sample is ashed with sulfuric and nitric acid, neutralized, and filtered. The filtrate is then polarographically analyzed in three electrolytes: ammonium sulfate, ammonia-ammonium buffer, and finally the ammonia buffer containing added disodium ethylenediaminetetraacetate (EDTA). The EDTA chelates cadmium, nickel, and zinc; this causes a shift in the reduction potentials of these metals to very negative potentials. In this way, they will not be reduced near the Pb wave.

Pulse polarography was applied to the measurement of lead (Ref. 20). Pulse anodic stripping with the Princeton Applied Research Corporation Model 174 Polarographic Analyzer was used to analyze Princeton tap water. The tap water sample was not pretreated, and supporting electrolyte was not added. The lead content was found to be 3 μg/l. A square-wave polarograph was used to determine trace amounts of lead in potable water as part of a pollution study in the vicinity of Iowa City, Iowa. Pb contents as little as 2 ± 0.32 μg/l could be determined without preconcentration of the water samples (Ref. 21).

Anodic stripping analysis using a rotating cell has been applied to the electrochemical analysis of lead in laboratory prepared water samples. The rotating cell is an electrocell manufactured by McKee-Pederson Instruments. Essentially, it is a cylinder closed at the bottom and partially open at the top which is rotated initially in one direction. The centripetal force causes the sample solution to lie in a thin film on the wall of the cylindrical electrode so that dissolved oxygen is removed in 75 seconds or less with a strong jet of nitrogen. After this sparging the cell is switched to its periodically reversing mode of operation. This applies a very efficient stirring action during which time the amalgam is accumulated at a potential more negative than that of the lead. After the amalgam accumulation step, the cell motor is switched off and the amalgam is stripped using an anodic voltage ramp and, simultaneously, the resulting peak current is recorded. The electrocell permits the analysis of lead at the 0.1 μg/l level within 10 minutes total analysis time (Ref. 22).

In summary, classical polarographic methods have have been applied to lead in water. The rotating electrode method which can measure lead at the 0.1 μg/l level in laboratory prepared solutions should be evaluated for application to water samples. The detection limit is lower than that of atomic absorption using extraction and the possibility of multielement analysis is attractive.

5. Activation Analysis

Application of photon activation analysis to nine elements was reviewed recently. Reported sensitivity for Pb in PbO was 4.87-127 cpm/μg (Ref. 23). Recent applications of activation analysis for the determination of lead include the determination of lead in paint with fast neutrons using a californium-252 source (Ref. 24). The method may have merit for analyzing the lead content of solid samples such as bottom sediments and suspended matter by dispensing with lengthy chemical treatments needed for bringing the solid samples into solution and would also have the potential for largely automating the determination of lead. The samples were packaged in a polyethylene snap-cap vial of 1 cm. diameter and 2-1/2 cm length. This was placed in a larger polyethylene vial with spacers to insure that the sample is in a position of maximum neutron flux. The fast neutron flux from the californium-252 source was approximately 5 x 10^7 neutrons/cm^2 sec. National Bureau of Standards SRM Pb paint was used. Paint samples were irradiated for one to two hours and after transfer to a clean counting vial were examined with a NaI(Tl) detector and a multichannel analyzer. Analyses were carried out at the National Bureau of Standards CF-252 facility which consisted of eight sample sources of 75 μg each. The sources were mounted in a 90 x 90 x 210 cm high aluminum tank filled with demineralized water. The photopeaks of the lead isotopes could not be resolved with the NaI detector; with a Ge(Li) detector, however, all three gamma lines of ^{204m}Pb could be adequately resolved.

The determination of lead with charged particle activation analysis was recently studied using proton, deuteron, and helium-3 activation using the 88-inch Texas A & M University variable energy cyclotron (Ref. 25). Irradiation energies used were 20 Mev for deuterons, 20 Mev and 30 Mev for protons, 40 Mev for ^{3}He and 40 Mev and 50 Mev for ^{4}He ions. Beam intensities were limited to 3 to 4 μA/cm^2 to preserve sample integrity. Analyses were performed using high purity glasses doped with 61 trace elements issued by the National Bureau of Standards (SRM's 610-616). High-purity metals obtained from Materials Research Corporation, Orangeburg, New York, were also examined. Thick targets of lead metal were used as standards. Flux monitors were copper foils (30 μm thick), iron foils (30 μm thick), and mica (muscovite foils ~ 25 μm thick). For total lead determination, techniques with sub-mg/l detection limits can be devised using the methods described in this paper with each of the four different activation modes examined. Deuteron activation appeared to offer the most versatility with possibilities for very rapid part-per-thousand level analyses, nondestructive or destructive sub-ppm determinations, and for measuring ^{204}Pb/^{206}Pb ratios under conditions providing maximum sensitivity (Ref. 25).

6. X-ray Methods

Lead and some other metals (e.g., Fe, Mn, Zn, Cu, As, Cd, Se) were measured in water at concentrations as low as a few mg/l using x-ray fluorescence. The metals were precipitated from the water with a carrier of the metals by either diethyldithiocarbamate or 1-(2-pyridylazo)-2-napthol and filtered. The precipitate collected on a filter was then analyzed for the metals content (Ref. 26).

Recent work on trace metal analysis in water using x-ray emission analysis utilized proton-induced x-ray emission (Ref. 27). Extensive x-ray emission studies were done primarily for lead, mercury, and cadmium. In this method the target to be analyzed was placed in the path of a beam of protons produced by a 3-MeV Van de Graaff accelerator. The atoms of the target are thus excited and emit characteristic x-rays which are captured by a solid-state detector. A pulse-height analyzer was used to count the x-rays and an energy spectrum is obtained. This method has advantages over conventional x-ray fluorescence spectroscopy in that there is little interference from bremsstrahlung or white radiation and that the x-ray production cross-section is larger. The targets were membranes which were impregnated with a cation exchange resin. The membranes, when placed in a solution or a stream containing metal ions, absorb the ions, thus acting as a preconcentration device. Since the equilibration time is long, the membrane tends to average out "pulse", or short-term events which do not reflect the actual overall-average distribution of metals in the sampled water system.

The ion-exchange membranes were obtained commercially (Type MC-3142, Ionac Chemical, Birmingham, NJ) and were used without further treatment. *In vitro* samples were prepared by equilibrating 6 x 20 mm pieces of membrane in 1000-ml quantities of solutions of the lead cadmium or mercury which were to be studied. These solutions were made up with deionized and glass-distilled water. *In situ* samples were prepared by placing the membrane in a lucite holder which was suspended in the water supply of interest for several days. The membranes were rinsed with distilled water and dried at 120°C in air prior to analysis.

C. SUMMARY AND CONCLUSIONS

Presently used standard methods to monitor lead-in-water are principally either atomic absorption or molecular absorption. The atomic absorption method usually requires extraction of lead as a complex into methylisobutylketone solvent, followed by aspiration into an air-acetylene flame. Direct aspiration is possible if the lead concentration falls in the range 1-10 mg/l. The molecular absorption method using dithizone is neither specific nor sensitive for measuring lead in fresh water, but is made both sensitive and selective by extraction methods.

The main difficulties associated with the monitoring of lead-in-water are lack of sensitivity and selectivity of the presently used methods. Anodic stripping plasma emission spectroscopy, and neutron activation analysis appear promising for use in analyzing for lead at the µg/l level and have the advantages of multiparameter capability.

D. ACKNOWLEDGMENT

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D.4. CONTENTS FOR
MERCURY-IN-WATER
MONITORING INSTRUMENTATION

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A. INTRODUCTION

Since 1969, much attention has been directed to mercury in the environment, and consequently, much has been learned. The public recognition of mercury as a potential health hazard followed reports of numerous incidents of human and wildlife illnesses and deaths traceable to ingestion of organomercury compounds. As a result of this awareness, there arose several excellent reviews of mercury in the environment (Ref. 1-15) and a valuable bibliography (Ref. 16). This introduction is intended to acquaint the reader with mercury in the aquatic environment, and how it can directly affect man.

The nature of environmental mercury is frequently misunderstood. Authorities differ widely in their attitudes from firm complacency to frenzied alarm. See Section 4 on Toxicology.

Firstly, even background (natural) concentrations exceed guidelines in some cases. Tuna and swordfish caught in unpolluted waters near Malaya and Africa had mercury concentrations exceeding the Food and Drug Administration guideline of 0.5 ppm (Ref. 10). The air above ore deposits may contain as much as 20 $\mu g/m^3$ of mercury (Ref. 5), higher than the Environmental Protection Agency's recent suggestion of 1 $\mu g/m^3$ maximum for public, long-term average exposures (Ref. 17).

Secondly, as a result of man's activities, mercury concentrations can be elevated above background levels, unsafe conditions created, and natural hazards enhanced. Liquid wastes can induce high levels of mercury in local waters and wildlife. Perch caught upstream from a pulp and paper mill outfall contained from 0.18 to 0.70 ppm mercury; those caught downstream from the outfall contained 1.90 to 3.02 ppm mercury (Ref. 1). Whitefish, pike and walleye were found to contain 0.10-9.00 ppm of mercury (Ref. 18). Mercury discharged into Minamata Bay in Japan was taken up by fish and entered the human food chain. The result was the death of 50 people directly related to eating the contaminated fish (Ref. 19). Other foods more commonly ingested than fish in the United States do not appear similarly contaminated with mercury, as shown by the data in Table 1 (Ref. 20). Similarly, uncontrolled plant emissions into air and water can cause the surrounding ambient air to contain average mercury concentrations over 1 $\mu g/m^3$.

Thirdly, because of the mobility of mercury, discharged mercury does not remain localized. Through natural cycles, it slowly disperses and extends itself into much broader regions to remain almost indefinitely.

1. Characteristics

Mercury is extremely mobile in the environment. Natural cycles transform and transport mercury throughout air, water, and soil. Elemental mercury is constantly outgassed from soil (Ref. 13). Mercury in the bottom sediment of waterways is converted by anaerobic bacteria into methyl mercury (Ref. 19), which can then be taken up by fish and enter the human food chain. In the atmosphere, many mercury compounds decompose in the presence of sunlight to form elemental mercury. Nearly all forms of airborne mercury can be washed out by precipitation and returned to the surface. Because

TABLE 1.

Concentrations of Mercury in Common Foods. All Results Are Given for Material as Received (Ref. 20).

Food	Samples Analyzed (No.)	Minimum Detectable Amount of Mercury (ppb)	Number of Samples with Mercury Content Below the Detection Limit	Mercury (ppb)	
				Range	Median
Flour*	28	3	25	< 3-6	< 3
Milk, dry*	33	4	13	< 4-27	10
Milk, whole	32	1	23	< 1-9	< 1
Sugar*	22	3	17	< 3-10	< 3
Potatoes	33	1	14	< 1-15	3
Beef	23	2	9	< 2-7	3
Chicken	24	1	9	< 1-7	3
Shrimp	32	2	0	5-43	14
Liver	22	2	11	< 2-8	3
Eggs	33	2	30	< 2-5	< 2

*Not freeze-dried.

mercury is readily cycled among air, water, and soil, any contribution anywhere is potentially an addition to the mercury pollution problem.

The processes and rates of mercury removal, which are presently unknown, are an important area of future research. Up to a century may be required for the removal of mercury from bottom sediment (Ref. 19).

The occurrence of aquatic mercury may be classified into three general and overlapping categories: background, discharged, and public. Background concentrations in the aquatic environment do not seem to warrant close attention. The natural level of mercury in water in the northeastern United States is said to be 0.06 ppb (Ref. 8). Mercury ranged between 0.05 to 0.11 ppb in water in western Canada (Ref. 9). The U.S. Geological Survey analyzed the concentration of mercury in a number of rivers in the United States in 1970. Mercury was reported as 0.1 ppb in most rivers and streams (Ref. 4).

Discharged sediment levels in many locations may be significantly higher than background levels. Since 1970, substantial decreases in discharges of mercury have taken place, and this may be reflected by a lower level of discharged effluents. Sediment immediately downstream of a chloralkali plant in Saskatoon (Canada) was reported in 1971 to contain 1800 ppm of mercury (Ref. 9). Sediment in Lake Ontario near Hamilton Harbor contained 692 ppm of mercury (Ref. 9). The concent of mercury in some water samples ranged from 0.99 - 10.4 ppb (Ref. 21).

The occurrence of mercury in man's food chain is of primary concern. This introduction of toxic organomercury compounds into man's food chain is documented for fish (Ref. 1; 16) and pigs (Ref. 19).

2. Forms of Mercury in Water

The term "mercury" is conventionally applied to all forms of the element mercury. In an aquatic environment, mercury may exist in the elemental, +1 or +2 oxidation states. For example, it may exist as $HgCl_2$, $Hg(OH)_2$, HgClOH, Hg, or methylmercury (Ref. 22, 23). Mercury compounds may also adsorb onto suspended matter and sediments.

Regardless of form, results of mercury analyses are reported on the basis of $\mu g/\ell$ (ppb). The form of the measured mercury may or may not be stated, although such information is important in terms of toxicological effects.

Mercury in fish exists primarily as methylmercury (Ref. 12, 22); the form so toxic to man if ingested in amounts exceeding about 1 mg/day (Ref. 12, p. 525).

3. Sources and Controls

Sources of mercury in the aquatic environment are included in Reference 16, p. 35. The sources include discharged effluents from chloralkali plants, wood pulp mills (Ref. 12, p. 519), and possible municipal wastes (Ref. 9). See Table 2.

TABLE 2.

Sources and Uses of Mercury (Ref. 12, p. 519).

The multiplicity of uses of mercury (over 3,000) creates many sources of contamination, and thus a diverse number of routes mercury compounds may take in reaching the environment. A survey of these sources is revealing. A partial list of mercury users in indicated below.

a. Electrical industry is the largest consumer in the U.S. (26.6%).
b. Chlor-alkali industry closely follows (23.1%). However, in Canada the chloralkali industry is by far the largest user.
c. Industrial control equipment--mercury switches, relays, etc. (10.6%).
d. Paints--bactericide fungicide for damp and humid conditions (14.4%).
e. Agriculture--fungicides (4.6%).
f. Dental preparations (4.1%).
g. Pulp and paper industry--fungicide and preservative (0.6%).
h. Catalysts in chemical manufacturing processes (2.5%).
i. General laboratory uses--hospitals, universities, and private labs.

Prior to July 1970, 50 plants were dumping 130 kg (287 lb) of mercury per day into U.S. waterways; by September 1970, this was reduced to 18 kg (40 lb) (Ref. 8). Methods used to control mercury discharges into the aquatic environment are discussed in Ref. 16, 19, 24, 25. The methods include precipitation (or cementation) of mercury by a more active metal -- e.g., aluminum, copper, iron, zinc. This is effective, but it substitutes another metal in solution usually in considerably more than an equivalent amount. Methods based on the precipitation of mercuric sulfide suffer from the high toxicity and offensive odor of sulfide reagents. Sorption of mercury on preformed metal sulfides--e.g., iron sulfide, cadmium sulfide, zinc sulfide--is an effective removal method. However, the mercury in solution is replaced by another ion (Ref. 24).

4. Toxicology

The toxicological effects of mercury on man depend to a large extent on the form of mercury ingested. Elemental, liquid mercury "is not a poison; a person could swallow up to a pound or more of quicksilver with no significant adverse effects...." (Ref. 4). Calomel, primarily mercurous chloride (Hg_2Cl_2), has been used medically as a cathartic, diuretic, antiseptic and anti-syphlitic (Ref. 26). Mercuric chloride ($HgCl_2$) is poisonous when taken orally and in a substantial dose (Ref. 4, 26). Organomercury compounds including the methyl and ethyl compounds can be lethal to man (Ref. 4, 19).

Inorganic mercury compounds, phenylmercury, and methoxyethylmercury are converted in the blood to soluble inorganic mercury salts (Ref. 1, 59). Carried by the blood plasma, the mercury is widely distributed to all tissues, but accumulates primarily in the kidneys and liver prior to excretion (Ref. 1, 59). Some accumulation of mercury salts also occurs in the brain, spleen, and alimentary tract (Ref. 59). Nonalkyl mercury might to a limited extent be transformed into methylmercury within the liver (Ref. 1, 11). In general, those compounds which are or readily form water-soluble inorganic salts are among the least toxic of the mercury compounds.

The more stable organic mercury compounds, notably alkyl mercury, are not readily converted to inorganic salts (Ref. 1, 59). Methyl and ethyl mercury, which are lipid soluble, are carried and stored for extended periods in the blood cells (Ref. 1). Because water soluble salts are not readily formed, little alkyl mercury is found in the blood plasma and excretion does not proceed readily through the kidneys. The stability and lipid solubility of the alkyl mercury compounds allow them to penetrate into cells more easily and to be retained much longer. Accumulation in the brain and liver is more pronounced than with other mercury forms. Methyl mercury is known to accumulate also in the fetus. Excretion appears to occur mainly via the liver into the feces; over 90%, however, can be reabsorbed as the feces pass through the gastrointestinal tract (Ref. 1). Some conversion of alkyl to inorganic forms does occur in the kidneys (Ref. 59), liver (Ref. 59), and intestine (Ref. 11). The excretion rate of methylmercury is slow, requiring about 70 days to remove half the accumulated amount (Ref. 12). Its mobility, retentiveness, and preferential concentration in the brain make alkyl mercury among the most toxic of mercury forms.

Elemental mercury has transport and retention properties resembling both inorganic and alkyl mercury compounds. Converted to mercury salts, it is partially transported in the blood plasma. Being somewhat lipid soluble, elemental mercury is also transported in the blood cells. While able to penetrate all body tissues, it accumulates in the brain, other nervous tissue, intestinal tract, and salivary glands (Ref. 1).

The toxicity of mercury is attributed to its high affinity for sulfur-containing compounds and its lesser affinity for organic ligands (Ref. 59). Interference by mercury in the synthesis and function of enzymes and other proteins can result in a variety of adverse effects (Ref. 59).

Alkyl mercury poisoning has somewhat different characteristics than other mercury poisoning. Symptoms may be dormant for weeks or months after acute exposure, and if brain damage occurs, effects may be irreversible. Inhalation of alkyl mercury can produce dryness and irritation in the nasopharynx and mouth. Alkyl mercury poisonings have caused permanent neurological damage resulting in impaired vision and hearing, sensory loss in limbs, ataxia, and tremor. Neurological disorders such as mental retardation and convulsive cerebral palsy have occurred in infants whose mothers were exposed to methylmercury during pregnancy (Ref. 1, 59). Fetal nerve tissue may be especially sensitive to methylmercury (Ref. 11).

Ingestion of 1.0 to 2.0 g mercuric chloride is frequently fatal to human beings (Ref. 28, p. 216). It produces corrosion of the intestinal tract, injury to the kidney, and ultimately death due to kidney failure (Ref. 4). The effects of some other mercury compounds are described in References 26 and 28. The kidney appears to be the concentrator organ for inorganic mercury (Ref. 29).

The mercury content in human urine is normally "zero", but may rise to 20 ppb in persons with amalgam dental fillings (Ref. 29). Persons given a mercurial diuretic had urine specimens containing 20 ppb mercury or above (Ref. 30). A hazardous exposure is believed to exist when urinary excretion reaches 250 ppb (Ref. 29). Two children exhibited symptoms of pink disease with urinary mercury excretions of 2000-5000 ppb (Ref. 30).

5. Health Standards

A limit of 0.5 ppm (500 ppb) of mercury in fish to be consumed by humans has been set by the Food and Drug Administration (Ref. 8). Departments of industrial hygiene usually consider 50 ppb of mercury in urine as indicative of excessive exposure (Ref. 30). A tentative standard for mercury in drinking water was set at 5 ppb by the U.S. Public Health Service in 1970 (Ref. 1, p. 28). A Swedish toxicological committee recommended a maximum acceptable intake level of 0.030 mg/day of methylmercury for a 70 kg (154 lb) male (Ref. 12, p. 525).

B. INSTRUMENTAL METHODS

The following discussion covers the literature to December 1972. Review articles containing sources of information on mercury analysis in water are included in Atomic Absorption Newsletter, Analytical Chemistry, and Chemical Abstracts. The Analytical Quality Control Laboratory of the EPA has a section on mercury analysis in water in Methods for Chemical Analysis of Water and Wastes, 1971.

1. Atomic Absorption Methods (AA)

Atomic absorption spectrophotometry is discussed briefly in the Introduction, Section C.2.1. Improvements in the atomic absorption methods have been incorporated into the analytical procedures for mercury as they are developed.

Mercury concentrations in water are often too low for direct analysis using flame AA. To compensate, a large volume of sample may be taken, or mercury may be concentrated by solvent extraction, amalgamation, absorption, or ion-exchange.

In the widely used Hatch and Ott method, potassium permanganate is added to a water sample contained in a bottle to convert mercury to the inorganic mercuric form. Excess permanganate is removed by addition of hydroxylamine hydrochloride, and mercury reduced to the elemental form by addition of stannous chloride. An air stream is directed through the sample solution to serve as a carrier gas for the mercury which is swept out as a vapor. The vapor is then passed into an absorption cell where the 253.7 nm Hg line emitted by a UV (ultraviolet lamp) is absorbed by the vapor. The mercury in the sample is totally converted to the atomic form; the sensitivity is increased substantially over that of the conventional flame technique where only a small fraction of the mercury is converted to the atomic form.

The Hatch and Ott method was modified in the EPA method to include oxidation with potassium persulfate to ensure complete oxidation of some organomercury compounds (Ref. 33, p. 121). Other modifications utilize addition of sulfuric and nitric acids to destroy residual organics (Ref. 34), and use of helium as the carrier gas (Ref. 44).

In the method by Moffitt and Kupel, biological and aquatic samples are decomposed with nitric acid, and mercury ions reduced to mercury metal using stannous chloride (Ref. 29). The mercury is swept out of solution by an air stream, and absorbed into charcoal. The charcoal is then introduced into a small boat-shaped tantalum vessel, which is inserted directly into an oxidizing air-acetylene flame. The minimum detectable quantity of mercury by this method is 20 nanograms. See Figure 1.

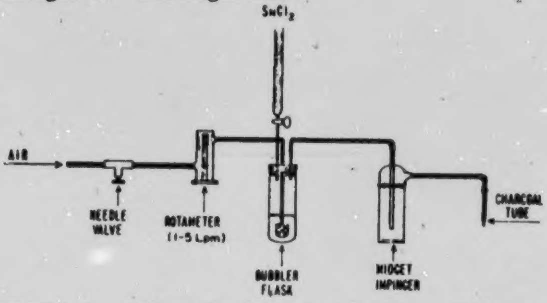

FIGURE 1. Schematic diagram of test apparatus (from Ref. 29).

Chau and Saitoh used a combination of solvent extractions and flameless atomic absorption (Ref. 32). Mercury in water samples was extracted with dithizone dissolved in chloroform. Dithizone has been found to react with some organomercury compounds as well as inorganic forms. The dithizone extraction also serves to concentrate the mercury in the smaller chloroform volume. Following dithizone extraction/concentration, the mercury was extracted back into an aqueous solution; stannous chloride was added to reduce mercuric mercury to the metal, and measurement made using flameless AA. A sensitivity of 0.008 ppb (8 ppt) was achieved using this technique.

Other methods for analyzing mercury in water utilize amalgamation of mercury onto copper or silver collectors. In one fell swoop, this method can be used to simultaneously separate, concentrate and convert various mercury forms from water samples (Ref. 21, 37-40). In these methods, the copper or silver wire is electrically heated to drive off collected mercury as a vapor. The mercury vapor is then passed into the optical cell where the change in intensity of the 253.7 nm Hg line is measured.

Collection of mercury on the wires is done either as a heterogeneous chemical reaction or as electrodeposition under an applied potential of 3 volts. Less time may be needed for electrochemical collection: 20 minutes versus two hours in one case (Ref. 37). However, if other metals are present in the water, they may also plate out, and interfere with the mercury analysis. The method can be applied to measuring concentrations at the nanogram level in laboratory prepared samples.

Other flameless atomic absorption methods of collecting and simultaneously concentrating mercury from aqueous samples onto solids include absorption of mercury vapor into charcoal (Ref. 29), and evaporation on a tantalum boat (Ref. 31). The procedure in Reference 31 involves extraction of mercury from urine samples into an organic layer, followed by evaporation of the organic layer (methyl isobuytl ketone) onto a tantalum boat. The boat is heated in the flame, and mercury measured as the vapor.

2. Emission Spectroscopy

Conventional emission spectroscopy is not sufficiently sensitive for direct measurement of mercury in water samples (Ref. 41). Methods involving plasma excitation sources do have the required sensitivity, and have been applied (Ref. 41, 43). Another method utilizes a dc discharge on samples of mercury vapor which were generated from water samples by reduction with sodium borohydride (Ref. 44). In this last method, volatile mercury compounds can be separated and analyzed using a gas stream and rubber diaphragm. Only volatilized mercury diffuses through the diaphragm, so that both free and total mercury can be analyzed in the same sample.

The above methods can have sensitivities in the parts per trillion (10^{-3} μg/ℓ) range.

In the April and Hume procedure (Ref. 41), 10 ml of sample solution is constantly aerated with helium. After the base line is stable, 0.5 ml of 2% titanous chloride in 1 M H_2SO_4 is added to reduce mercury to elemental form. The purging of elemental mercury by the helium stream into the helium plasma causes an emission maximum in about 20 seconds. The emission, monitored by a conventional monochromator-photomultiplier tube, is linearly proportional to the mercury concentration from 0.001 to 1 μg/ml. The detection limit might be as low as 0.0002 μg/ml in the 10 ml sample, lower than the 0.001 μg/ml limit in the Hatch and Ott flameless atomic absorption procedure (Ref. 60). Ag, Pd, and Au interfere if present in concentrations 100 times greater than mercury. Pb, Cd, Zn, Cu do not interfere in concentrations 1000 times greater than mercury. Concentrations of Cl^- over 0.1 M cause a slight depression. Phenyl and methylmercury can be analyzed by the same procedure. Elemental and dimethyl mercury are immediately aerated by the helium stream before addition of reductant unless oxidized to less volatile forms. The plasma torch unit is not commercially available but could be constructed for under $1000.

SpectraMetrics, Inc. has introduced argon plasma emission spectrometers which should be applicable to the April and Hume procedure for mercury. Detection limits have not been indicated but might be comparable to helium plasma instruments.

In a method by Braman for measuring mercury in solution (Ref. 44), the mercury is reduced to elemental form with $NaBH_4$ solution and allowed to diffuse through a latex or Saran Wrap membrane into a helium carrier stream; the mercury is excited as it is carried through a 900 V, 31.5 watts/inch dc discharge. A monochromator and photomultiplier tube measure the 253.7 nm emission intensity. With 200 ml of sample solution in an open beaker and a latex membrane area of 12 cm^2, the limit of detection is 4 x 10^{-6} μg/ml mercury. Analyses performed on natural water samples demonstrated measurements of 1 - 16 x 10^{-5} μg/ml (ppm). Dimethyl mercury could be determined without reduction, with the same sensitivity as elemental mercury. Oxidation during pretreatment has been successfully done with $KMnO_4$-H_2SO_4. The method has since been applied to determination of nanogram quantities of arsenic and antimony (Ref. 57).

Emission spectroscopy is less susceptible than atomic absorption to interference from aromatics, since aromatics do not usually emit in the 253.7 nm region. But as in atomic absorption, cobalt is a potential interference, as it has an emission line at 253.649 nm, close to the mercury line at 253.652 nm (Ref 61). The cobalt problem is avoided if the mercury is selectively removed such as in the Braman or the cold vapor method.

3. Neutron Activation Analysis

This technique was used to measure the total mercury content in fish (Ref. 46, 58), some common foods (Ref. 20) and samples of fresh water (Ref. 45). Data for the food analysis--shown here in Section A as Table 1--show that except for certain fish the major foods are essentially free of mercury.

In each of these analyses, mercury was separated using anion exchange or precipitation (Ref. 58). For example, the mercury in fresh water (Ref. 45) was converted to $HgCl_4^{2-}$ by adding sufficient HCl to a four-liter sample contained in a polyethylene bottle to make the final solution 0.1 N in HCl. The acidified water sample is passed through anion-exchange resin loaded filter paper to concentrate the Hg. The filter paper is allowed to air dry, sealed in Mylar bags and irradiated. Irradiation time was two hours, at a thermal neutron flux of 1.3 x 10^{13} n/cm^2-sec. The samples were cooled 3-4 days, transferred to a polyethylene bag and counted. Mercury in samples of fresh waters was found to range between 0.03-6.6 ppb. The detection limit of the instrument is calculated to be 0.005 μg Hg.

A sample of methylmercuriguanidine was analyzed by first treating for 30 min with chlorine gas to degrade the compound and convert it to an analyzable form (Ref. 45). Anion exchange followed by irradition showed that recovery was about 100% for the methylmercuriguanidine sample. Only 0.36% was recovered for samples which were not chlorine treated. Other organomercury compounds may possibly be analyzable using this procedure (Ref. 45).

The good sensitivity, precision and accuracy obtained by neutron activation analysis is shown in Table 3 (Ref. 20). The potential of neutron activation/anion exchange technique to distinguish between inorganically bound and organically bound mercury is indicated by the low recovery of the latter when chlorine pretreatment is not used (Ref. 45).

The precipitation method was used to measure the mercury content in bottom sediments as well as fish (Ref. 58). Sediment levels from Lake Erie at the mouth of the Buffalo River ranged from 1.95-6.79 ppm, on a dry weight basis. Mercury waste had been discharged into the Buffalo River prior to April 1970.

4. Automated Laboratory Analyzers

Laboratory automation of atomic absorption spectrophotometers was achieved by using a Technicon Auto-Analyzer (Ref. 36, 47, 49). One such system automates the Hatch and Ott method for mercury using the schematic shown in Figure 2. The rate of flow of the air

TABLE 3.

Analyses of Mercury Standards and of Samples by Neutron Activation (Ref. 20)

Material	Mercury (parts per million)	
	This work	Other work
NBS orchard leaves*	0.148 ± 0.010	0.155 ± 0.006 0.162 ± 0.010
International Atomic Energy Agency standard flour*	4.6 ± 0.5	4.87 ± 0.06 4.9 ± 0.3
Food and Drug Directorate flour No. 32573	0.011 ± 0.003	0.011 ± 0.004 0.007 ± 0.02
Swedish fish No. 410-30	1.29 ± 0.13	1.14 1.17
Swedish fish No. 410-28	2.16 ± 0.22	2.24 2.20
Bowen kale*	0.25 ± 0.03	0.23

*Standard material.

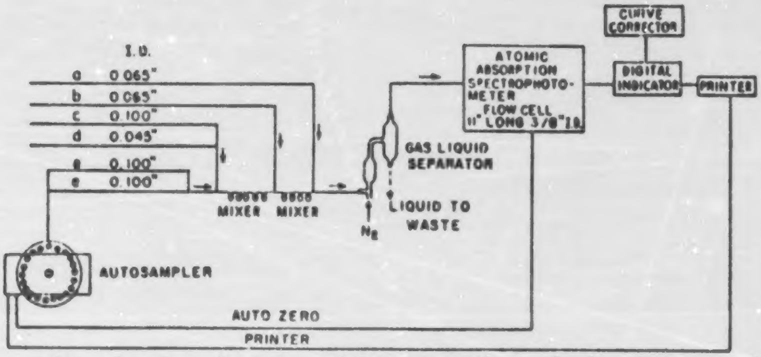

FIGURE 2. Schematic of equipment used for automatic analysis of mercury (Ref. 36).

a. 10% stannous chloride in 0.5N sulfuric acid
b. 3% hydroxylamine hydrochloride -- 3% sodium chloride
c. air
d. 5% potassium permanganate
e. sample

stream through the sample and to the absorption cell is critical; the sensitivity decreased with increasing flow rate.

It is possible to analyze 22-50 samples per hour (Ref. 36, 49). Comparative thruput for non-automated operation is not given, but automation should free the laboratory operator to do other work. Analytical results obtained for mercury in several types of sample matrices are shown in Table 4 (from Ref. 36).

TABLE 4.

Results of Duplicate Analyses by Automated Procedure and Comparisons with Manual Procedure (Ref. 36)

Sample	Hg concentration, ppm		
	I[a]	II[b]	III[c]
Brine 1	0.0077	0.0071	
2	0.0078	0.0076	
3	0.0041	0.0044	
Fish 1	0.07		0.06
2	0.4		0.4
3	0.8		0.6
4	1.2		1.0
Blood[d]	0.055		
	0.062		
Coal[d]	0.48		
	0.45		
	0.50		
	0.52		

[a] I. Automated procedure.
[b] II. Beckman Mercury Vapor Monitor (Industrial Lab).
[c] III. Beckman Mercury Vapor Monitor (Government Lab).
[d] Replicate analyses.

5. Continuous or Periodic Analyzers

Continuous analyzers can be used in the field to sample and analyze mercury in water unattendedly. The Olin Mercury Monitor for Liquids and the Geomet Model 103 are commercially available for analysis of mercury in water.

The Olin Mercury Monitor for Liquids measures total mercury. A programmer sets the following sequence of instrumental functions. See Figure 3. A pre-determined volume of 10% hydrazine solution is added to the scrubber via the reagent loop. A fixed volume of catalyst solution (0.5% cupric chloride dihydrate, 3% potassium persulfate, and 2% sulfuric acid) is then added to the filtered sample in the sample loop. Mercury-free air is bubbled through the reagent mixture until the reading of the UV detector has stabilized. An automatic servomechanism subsequently zeroes the recorder. The fixed volume of sample is then discharged into the reagent medium. The resulting elemental mercury is purged from the liquid by the air stream through the pyrolyzer and into the UV photometer tube for detection and measurement. The pyrolyzer is set at 900°C and serves to destroy possible organic impurities that may absorb UV light. It also favors formation of halogen acids rather than non-absorbing mercury halides.

The detection limit of the Olin monitor for liquids is given as 0.3 ppb. The mean

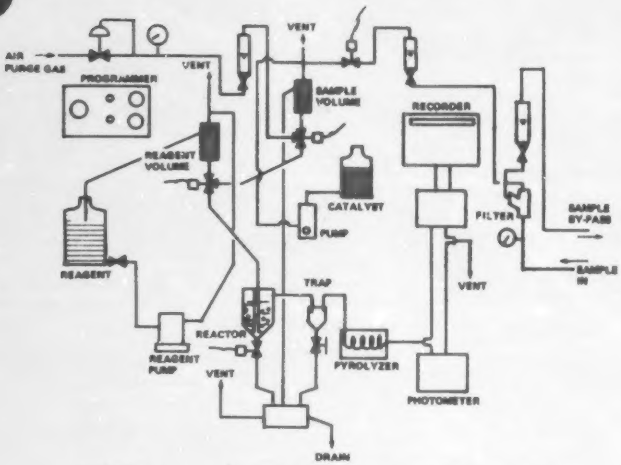
AIR
PURGE GAS
PROGRAMMER
VENT
VENT
SAMPLE VOLUME
RECORDER
REAGENT VOLUME
CATALYST
PUMP
FILTER
SAMPLE BY-PASS
SAMPLE IN
REAGENT
TRAP
VENT
REACTOR
REAGENT PUMP
VENT
PYROLYZER
PHOTOMETER
DRAIN

FIGURE 3. Schematic Diagram of Mercury in Liquid Monitor (Olin) (Ref. 35).

deviation was ±0.178 ppb for sample concentrations at the 7.5 ppb level. The analysis cycle time is six or more minutes.

The Geomet Model 103 Mercury Air Monitor utilizes a modular attachment for applications to water monitoring. The Geomet Module 201 provides for extraction of Hg from all forms of effluent waters, which can then be sampled by the Model 103 air monitor. See Figure 4.

The sample from the water module is passed over two consecutive precious metal wire grids which collect the Hg. At the completion of the sampling pre-measurement concentration period, the grids are serially heated to vaporize the collected Hg into the UV detector cell.

6. Other

Nanogram quantities of mercury have been measured by flameless atomic fluorescence in a variety of samples including water, rock, wheat, flour and natural sediments (Ref. 40). The advantages of atomic fluorescence over atomic absorption are said to include better sensitivity and lesser requirements for instrumentation. Sample pre-measurement handling utilized mercury oxidation/reduction techniques, followed by collection of the vapor onto silver. The resulting silver amalgam was then heated to release the mercury vapor into the fluorescence cell for subsequent measurement.

Picogram (10^{-12} gm) quantities of mercury were measured in 1-10 mg samples using an x-ray fluorescence procedure (Ref. 48). In this method, liquid samples containing mercury are deposited on a tantalum strip that is then heated. The resulting mercury vapor is collected on a gold foil. A second heating releases the mercury to an inert gas mixture where it is measured by x-ray fluorescence.

Methylmercury present in fish tissue was analyzed by electron capture gas chromatography (Ref. 22). The methylmercury in the fish tissues were isolated as methylmercury chloride and purified. The purified material was determined by the gas chromatographic technique, using electron capture monitoring.

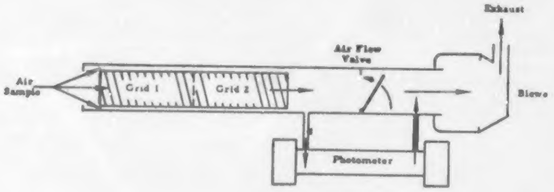
Exhaust
Air Flow Valve
Air Sample
Grid 1
Grid 2
Blowe
Photometer

FIGURE 4. Air flow schematic diagram (Geomet 103) (Ref. 56).

C. SUMMARY AND RECOMMENDATIONS

The development of new instrumentation systems for monitoring mercury using atomic absorption as the core is nearly always in progress. One might try to use combinations of existing methods, modifications of existing methods for mercury in air (as is done), or seek to find original techniques for mercury monitoring.

Halides and halogens might be effectively removed initially by silver wire heated to 450°C (Ref. 50), or by scrubbing the pyrolyzed air with 5% $SnCl_2 \cdot 2H_2O$, 1.2 N HCl solution as done in the Olin Air Monitor. In solution, any ionic mercury is quickly reduced to elemental form, and halides are retained in solution by reaction with tin(II) to form tin(IV) (Ref. 35). After scrubbing, the solution is aerated to release elemental mercury vapor into the photometer.

Besides through removal, interference can be minimized by comparison of the measured signal with a reference, or background, signal. Williston (Ref. 51) uses a common lamp to illuminate the sample cell and a reference cell; by passing the sample air through the sample cell, then a gold filter to remove elemental mercury vapor, and finally the reference cell, the difference between the absorption in the sample cell and that in the reference cell is a measure of the elemental mercury vapor concentration. In other words, the absorption by mercury and interferences minus the absorption by interferences equals the absorption by mercury. By using a common lamp, inaccuracies from differences between lamps or from small variations of lamp intensity are eliminated.

A reference signal indicating the absorption by interferences can also be obtained by measuring the absorption at wavelengths immediately adjacent to the 253.7 nm resonance wavelength. Broadband interferences would essentially absorb evenly across a short spectral interval while elemental mercury vapor would absorb only about the resonance wavelength. While a short interval spectrophotometer reading with an appropriate scale factor can be used for reference (Ref. 52), a much more refined technique taking advantage of the slightly broadened line emitted from a low-pressure or contaminated mercury lamp has been developed (Ref. 52). The band edges of the broadened line serve as the reference wavelengths, and the band center serves as the measuring wavelength.

This type of correction may also be accomplished by using Zeeman components which are generated by placing the mercury lamp source in a magnetic field. An instrument using the Zeeman effect from a constant magnetic field was developed by Hadeishi and McLaughlin (Ref. 54). See Fig. 5,6. Another instrument using the Zeeman effect is the Scintrex HGP-2 (Ref. 55) which applies a pulsed magnetic field to the mercury lamp source to obtain pulsed Zeeman components used as reference wavelengths. The elemental vapor concentration is measured as the difference between the absorptions at the 253.7 nm emission line and at the Zeeman components.

Preferential preconcentration of mercury is another technique for reducing interference. During a sampling period that can be up to 180 minutes, the Geomet Model 103 Air Analyzer (Ref. 56) collects elemental mercury by amalgamation onto precious metal grids. The grids are heated just prior to analysis, and the liberated burst of elemental mercury vapor is carried by sample air into the UV photometer.

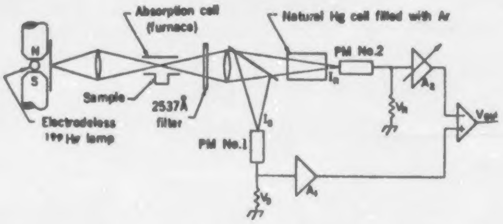

FIGURE 5. *Block diagram illustrating the principle of operation of the device (Ref. 54).*

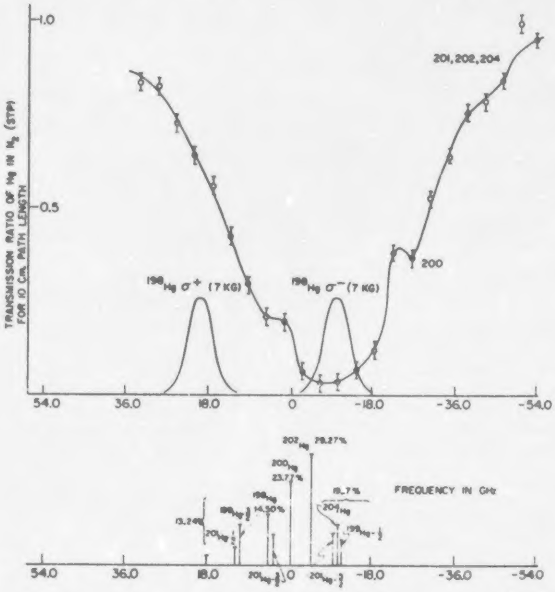

FIGURE 6. *Zeeman-shifted line profile of σ⁺ and σ⁻ of ^{198}Hg in 7 kG, superimposed on an absorption profile of naturally-occurring mercury in 1 atmosphere (STP) of N_2 (Ref. 54).*

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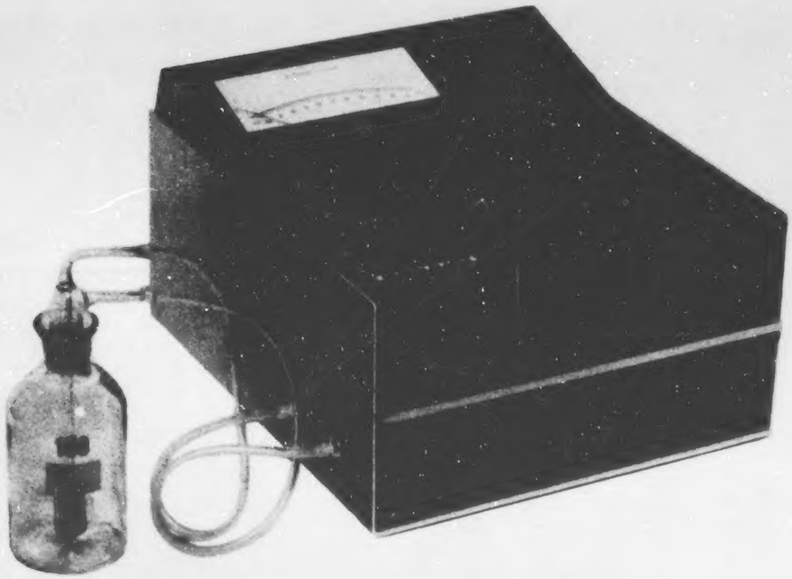
H2O-MET
Field: HG
Coleman 1
Sept. 1975

Mercury in Water Analyzer

Coleman MAS-50 Mercury Analyzer System



Class	Batch - Sampling
Categories of Water	Fresh, Waste, and Saline
Principle of Operation	UV (253.7 nm) Absorption: UV radiation from an Hg lamp passes through sample cell to phototube. Hg vapor reduces UV transmittance of sample cell and output from phototube. Sample may be introduced directly from the air or may be aerated from a solution treated with $KMNO_4$, followed by H_2NOH and $SnCl_2$ solutions.
Minimum Detectable Sensitivity	≤ 26 μg/m^3 in direct sampling for Hg vapor 0.01 μg Hg in 100 ml solution
Range	0-257 μg/m^3 in direct sampling for Hg vapor 0-0.28, 0-9 μg Hg in 100 ml solution
Interferences	
Multiparameter Capability	Suitable for Hg determinations in water, gases, food products, air, organic and inorganic wastes, biological samples (procedures available).
Sampling	Method: Continuous in direct air sampling. For water: batch in modified Hatch-Ott, ∿15 min per measurement. Volume: 100 ml prepared sample for standard procedure Maximum Temperature Input: Operates at room temperature Collection Efficiency: Not applicable Maximum Number of Sample Sources: See other parameters above

Performance

Accuracy: Sensitivity = 0.01 μg mercury.
Reproducibility: <±3% using standard solutions
Linearity: ±2% for 0-1 μg Hg in 100 ml solution; non-linear otherwise
Noise: Not applicable
Lag Time: 10 min
Rise Time: 40 sec
Retention Time: 20 sec
Fall Time: 30 sec
Zero Drift: Zero adjustment may be made prior to each measurement.
Span Drift: Span adjustment may be made prior to each measurement.

Operation

Ambient Temperature Range: 65° to 80°F
Temperature Compensation: Not available
Relative Humidity Range: 0-90%, approximate
Calibration: Performed during each measurement cycle. Zero adjustment is made when a partition is inserted between sample cell and phototube. Span adjustment is made when partition is removed and before sample is introduced.
Procedure: In direct sampling, air is drawn directly into instrument; a Scrubber Kit is necessary for zero adjustment. For a solution sample, additional apparatus for scrubbing is needed. The 100 ml solution sample is treated to digest the Hg and then to form elemental Hg. An aerator is placed in the elemental Hg solution. A pump circulates the air in a closed-loop through the solution and the sample cell.
Unattended Period: Not applicable. Instrument must be re-set between samples.
Maintenance: Supply reagents

Requirements

Power: 110/220 V, 50/60 Hz
Weight: 7.7 kg (17 lb)
Dimensions: 19 cm H x 29 cm W x 33 cm D (7.5" x 11.5" x 13")

Features

Output: Meter with peak holding possibility
Training: Average lab technician can operate. Directions & procedures included.
Options: Analysis reagents, mercury standard solutions, mercury scrubber to remove atmospheric Hg vapor, reagent dispensers and trays, chart recorder , micro sample apparatus

References

(a) Manufacturer's bulletin, B-350B-871.
(b) Manufacturer's price list (Aug. 1975)

Cost

MAS-50 Mercury Analyzer System	$ 1256.00
Mercury Analysis Reagent Kit	63.50
Reagent Tray	22.70
Mercury Scrubber Kit	12.60
Mercury Standard Solution (Concentrated)	13.90
Chart Recorder, Solid State, Multi-Range	1584.00

Remarks

All-plastic sample cell is easy to clean and inexpensive to replace. Peak holding circuit allows easy reading of meter for maximum indication.

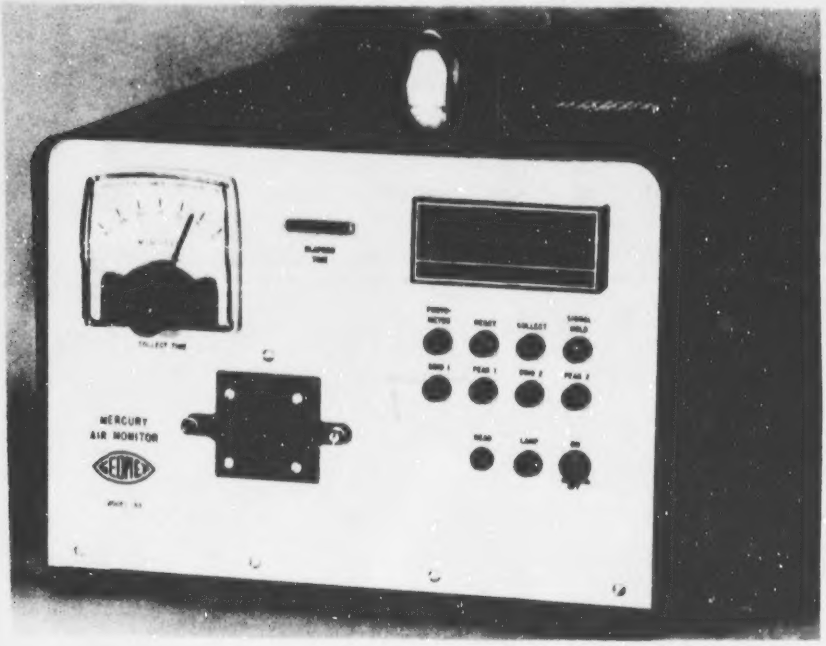
All above information supplied by the manufacturer.

Address

Coleman Instruments Division
Perkin-Elmer Corporation
2000 York Rd.
Oakbrook, IL 60521
(312) 887-0770/242-4050 Cable COLINST

Total Mercury in Water

Model 103 Mercury Air Monitor
(See: Module 201 Water Sampler, Geomet 2)



Class	Field or Laboratory: Batch - Sampling
Categories of Water	Fresh, Waste, Saline
Principle of Operation	UV (253.7 nm) Absorption: Air from the Module 201 Water Sampler is passed over two consecutive silver wire or gold-plated wire grids which collect HG vapor. At end of sampling period, grids are serially heated by an electric current to release the collected Hg vapor into the UV photometer sample cell. For total Hg monitoring, air sample is first passed through a catalytic converter module (Module 109) for conversion of Hg compounds to Hg vapor; converter contains Al_2O_3 pellets at 675°C (1250°F).
Minimum Detectable Sensitivity [a,e]	.001 $\mu g/m^3$ (30 min sampling period, 200 liter/min sampling flow rate)
Range [a,e]	.001-1000 $\mu g/m^3$ (30 min sampling period, 200 liter/min sampling flow rate)
Interferences	Appreciable (>10%) from Moderate (5-10%) from (See Remarks) Slight or none (<5%) from molecular species absorbing light at photometer wave length
Multiparameter Capability	None
Sampling	Method: Continuous (cyclic operation) - pump. Alternate sampling and analysis periods. Volume: 5, 20, 50, 100, or 200 liter/min during sampling; ~2.0 liter/min during analysis. If used with catalytic converter, ≤30 liter/min during sampling. Input Temperature Range: -23° to 93°C (-10° to 200°F) Collection Efficiency:

Performance

Accuracy: ±5%
Reproducibility: ±5%
Linearity: Non-linear output
Noise: Negligible[e]
Lag Time: Measurement cycle is 5 to 180 min. Sample period may be
Rise Time: up to ~180 min. Analysis period is 2 min.
Retention Time: Dependent on cycle time[e]
Fall Time: 5 sec[e]
Zero Drift: <0.1% per day[e]
Span Drift: <1.0% per day[e]

Operation

Ambient Temperature Range: -23° to 52°C (-10 to 125°F)
Temperature Compensation: UV lamp automatically controlled for intensity variations arising from temperature variations.[e]
Relative Humidity Range: 0-99%[e]
Calibration: Air samples saturated with Hg vapor are prepared in a stirred, thermostatted vessel. Aliquots are taken with a syringe and injected into the monitor.[b]
Procedure: Set length of sample period. When peak indicating light is on, read digital output meter. Correlate meter reading with calibration curve. After analysis, instrument automatically begins a new measurement cycle.
Unattended Period: >24 hours[e] (See Remarks)
Maintenance: Replace blower (pump) brushes ~1000 hours, blower bearings ~12 months, photodiode ~12 months, mercury lamp ~3000 hrs. Inspect above every 1000 hrs. Occasionally clean photometer windows every 1000 hrs. Clean collection grids as necessary by heating 200°-225°C for 8-24 hrs.

Requirements

Power: Model 103 Mercury Air Monitor, 115 V, 60 Hz, 2 kW
Module 109 Catalytic Converter, 115 V, 60 Hz, 12 A
Weight: Model 103, 15.9 kg (35 lbs)
Module 109, 13.6 kg (30 lbs)
Dimensions: Model 103, 25 cm H, 36 cm W, 46 cm D (10" x 14" x 18")
Module 109, 46 cm H, 30 cm W, 30 cm D (18" x 12" x 12")

Features

Output: Digital meter (arbitrary units); recorder connection with live zero output at 10.0 V - signals vary negatively from 10.0 V
Training: Minimal, manual provided
Options: Module 109 Catalytic Converter; gold plate on copper or gold plate on silver collection grid; corrosion resistant Model 104; remote sampling head Model 106; stack probes; moisture trap for stack probe.

References

a.) Manufacturer's brochure for Model 103 (received March 1972)
b.) Manufacturer's instruction and maintenance manual for Model 103 (Dec. 1971)
c.) Manufacturer's Price List (Feb. 1972)
d.) Manufacturer's brochure for Module 109 (received March 1972)
e.) Manufacturer's letter of June 13, 1972
f.) Manufacturer's letter of Nov. 20, 1972
g.) Manufacturer's communication, April 9, 1973.

Cost

Model 103 Mercury Air Monitor with variable 0-30 or 0-180 minute sample period timer and silver wire collection grid	$8,740
Model 104 Mercury Air Monitor, as above but with corrosion protected components	9,430
Module 109 Catalytic Converter	1,122
Collection Grid, silver	782
Collection Grid, gold plate or copper	863
Collection Grid, gold plate or silver	1,083
Stack probe with stainless steel lining Stack probe with Pyrex lining, 3 feet length Moisture trap for stack probe	price available upon request

Remarks

Flow rate during sampling is limited by the size of the air inlet orifice located on the front panel. The size is controlled by using orifice plates supplied with the instrument.

An instrument warm-up of 30 minutes is advisable, prior to utilization for data collection. In operations where absolute concentrations are desired, instrument calibration should be occasionally checked using either a hypodermic syringe sample or permeation tubes. The latter are very convenient field calibration sample sources, but each requires considerable care in preparation and initial calibration. (Comments in manual)[b]

Interferences minimized by use of two section grid collector technique which applies zero correction to each analysis, consisting of signal arising from any potential interference. (Comments by manufacturer)[e]

All above information supplied by the manufacturer.

Automatic reset of measurement cycle and the possibility of chart recorder readout allow possible unattended operation.

Address

Geomet, Inc.
50 Monroe Street
Rockville, MD 20850
(301) 762-5820

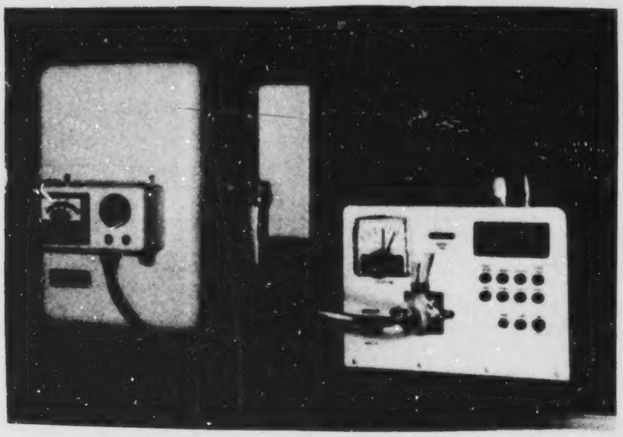
or

Geomet, Inc.
2814 A Metropolitan Place
Pomona, CA 91767
(714) 593-1318

H2O-MET
Field: HG
Geomet 2
Sept. 1975

Mercury in Water Sampler

Mercury Water Module 201



Class	Field or Laboratory: Batch - Sampling
Categories of Water	Fresh, Waste, Saline
Principle of Operation	Flash pyrolysis of incoming water sample followed by thermal decomposition to convert mercurials to elemental mercury. Module operates in conjunction with Geomet Model 103 Mercury Air Monitor.
Minimum Detectable Sensitivity	1 ppb
Range	1 ppb - 1000 ppm
Interferences	None
Multiparameter Capability	None
Sampling	Method: Continuous - pump Volume: 1-3 ml/minute Maximum Temperature Input: ≤48.9°C (≤120°F) Collection Efficiency: N/A Maximum Number of Sample Sources: 1 per analysis; Samples may be sequentially introduced with special valving.

Performance

Accuracy: ±5%
Reproducibility: ±5%
Linearity: Non-linear output
Noise: Negligible
Lag Time: { Measurement cycle is 5 to 180 min. Sample period may be
Rise Time: { up to ~180 min. Analysis period is 2 min.
Retention Time: Dependent on cycle time
Fall Time: 5 sec
Zero Drift: <0.1% per day
Span Drift: <1.0% per day

Operation

Ambient Temperature Range: 1 to 51.6°C (33 to 125°F)
Temperature Compensation: N/A

Relative Humidity Range: N/A
Calibration: N/A

Procedure: N/A

Unattended Period: >24 hours
Maintenance: Periodic removal of salt/residue trap; period dependent on salt concentration of incoming liquid sample.

Requirements

Power: 115 Vac; 60 Hz; 12 amps
Weight: 20.4 kg (45 lb)
Dimensions: 30.5 cm x 40.6 cm x 45.3 cm (12" x 16" x 18")

Features

Output:
Training: Minimal. Schematic provided.
Options: None.

References

1. Manufacturer's letter, November 20, 1972
2. Manufacturer's New Product Announcement, Module 201
3. Manufacturer's price list, 2/8/72, Rev. D
4. Manufacturer's communication, April 9, 1973.

Cost

Module 201	$3,910

Remarks

Address

Geomet, Inc.
50 Monroe St.
Rockville, MD 20850
(301) 762-5820

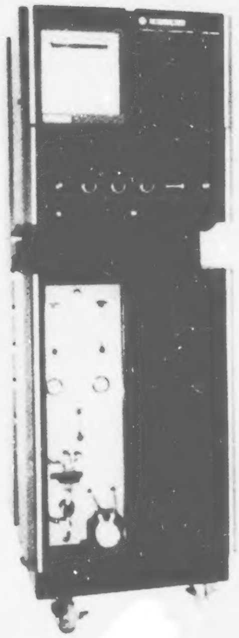
or

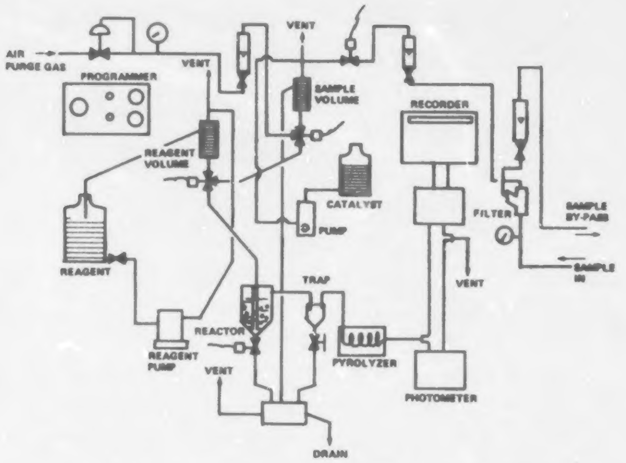
Geomet, Inc.
2814 A Metropolitan Place
Pomona, CA 91767
(714) 593-1318

H2O-MET
Field: Hg
Ionics
Sept. 1975

Mercury Continuous Analyzer

Ionics Mercury Monitor for Liquids




AIR
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RECORDER
CATALYST
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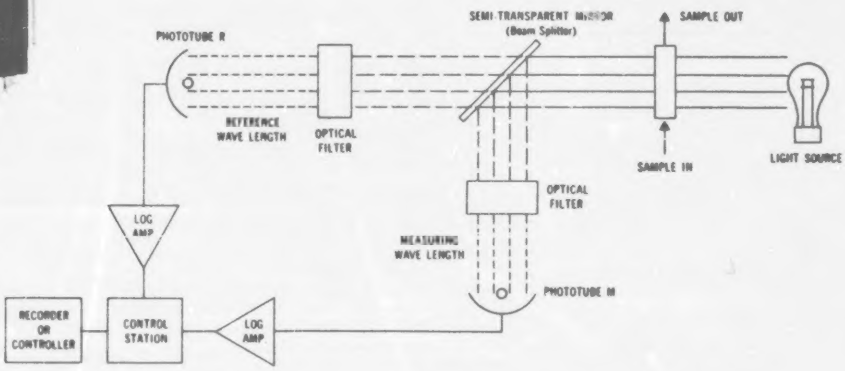
FILTER
SAMPLE
BY-PASS
SAMPLE
IN
REAGENT
VENT
TRAP
REACTOR
REAGENT
PUMP
VENT
PYROLYZER
PHOTOMETER
DRAIN

Schematic Diagram of Mercury in Liquid Monitor


PHOTOTUBE R
SEMI-TRANSPARENT MIRROR
(Beam Splitter)
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REFERENCE
WAVE LENGTH
OPTICAL
FILTER
SAMPLE IN
LIGHT SOURCE
OPTICAL
FILTER
LOG
AMP
MEASURING
WAVE LENGTH
PHOTOTUBE M
RECORDER
OR
CONTROLLER
CONTROL
STATION
LOG
AMP

Du Pont UV-400 Detector

Class	Continuous-Sensor, Stationary
Categories of Water	Fresh, Waste
Principle of Operation	Flameless UV absorption. Water sample reacted with potassium persulfate/copper chloride solution; then with hydrazine/colloidal copper solution to convert mercury forms to elemental mercury. Air bubbling system carries mercury as a vapor through a pyrolyzer, then to an absorption cell irradiated with mercury line from a mercury source. The decrease in intensity of the 253.7 nm line from the DuPont UV-400 is detected electronically, and taken as a measure of Hg in the sample.
Minimum Detectable Sensitivity	0.3 ppb

Range	0-3 ppb or higher as requested
Interferences	None, removed chemically or pyrolytically
Multiparameter Capability	None, measures only mercury of any form.
Sampling	Method: Periodic (analysis approximately every 6 minutes), automatic Volume: 10-20 ml, as required Maximum Temperature Input: Ambient, 4°C-50°C approx. Collection Efficiency: 100% Maximum Number of Sample Sources: 4
Performance	Accuracy: ±2% of full scale Reproducibility: ±0.178 ppb, for 7.5 ppb concentration level Linearity: 0-50 ppb, or higher as required Noise: ±2% of full scale Lag Time: ~6 minutes per measurement cycle Rise Time: Not applicable Retention Time: Not applicable Fall Time: Not applicable Zero Drift: Automatic zeroing is provided Span Drift: None
Operation	Ambient Temperature Range: 4°C-50°C approx. Temperature Compensation: Automatic zero compensates for temperature changes Relative Humidity Range: Saturated at ambient conditions Calibration: May be dynamic. Hg standard solutions must be prepared fresh. Procedure: Introduce calibration standards into monitor manually, or automatically using a pump. Unattended Period: 3-4 days between reagent changes Maintenance: Minimal. Supply reagents and carrier gas (air)
Requirements	Power: 115 V ac, 60 Hz Weight: Approximately 800 lb Dimensions: 76" x 26-1/8" x 32" (193 cm H x 67 cm W x 81 cm D)
Features	Output: 24 hour or strip-chart recorder. Leeds & Northrop Model H Recorder Training: 1-2 days on-site, as required Options: Multi-point sampling system, remote recorder
References	Manufacturer's brochure "Series 1900 Mercury Analyzers," 1975.
Cost	Model 1931 (single sampling point) $19,250. Model 1932 (double sample point) 20,150. (+ $300 for each additional channel up to 4)
Address	Ionics, Inc. Instrument Division 65 Grove St. Watertown, MA 02172 (617) 926-2500

H2O-MET
Laboratory : Hg
Spectro Products 1
August 1975

Mercury Analyzer
Model HG-3

Class	Semi-portable batch sample
Principle of Operation	Flameless Atomic absorption at 253.7 nm; multiple wavelength – time shared UV radiations are passed through a single absorption cell, through a custom filter, to a single detector. Two hollow cathode sources are used and the reference lamp is held constant by automatic gain control.
Sensitivity	0.05 µg Hg/ℓ in 4 ml sample (0.2 ng), <0.6 ng for 1% absorption
Range	0.2 ng - 20 µg
Interferences	In concentrations greater than: $CuSO_4$ 1.0 g/ℓ, Chloride 5000 mg Cl-/ℓ, Sulfide 20 mg/ℓ (Na_2S). Tolucne 500 µg/ℓ, Benzene 500 µg/ℓ, Ethyl Alcohol 0.5%, Methyl Alcohol 0.5%, Glycerol 0.5%, Chloroform 0.5%, Carbon Tetrachloride 0.5%; slight to none from dust and other UV absorbing substances; a dryer may be required if a great amount of H_2O is present.
Sampling	Method: Intermittent for solution reduction evolution Volume: 21.5 mℓ sample cell (24.5 cm long) Collection Efficiency: Method dependent
Performance	Accuracy: Dependent upon standards as per sample technique Reproducibility: ± 3% at 30 $\mu g/m^3$ and greater ±10% at 3 $\mu g/m^3$ Linearity: ±1% for 2 to 200 $\mu g/m^3$ Noise: ±0.1% for absorption Zero Drift: < 0.1% with manual adjust
Operation	Calibration: Manual introduction of serially diluted samples of mercury in solution Unattended Period: Method dependent Maintenance: Demountable cell cleaned or replaced as necessary (depends on sample condition); hollow cathode lamp 2500 hour MTBF
Requirements	Power: 115 V, 50/60 Hz, 60 Watts max Size: 31 cm H x 36 cm W x 38 cm D (12" x 14" x 15") Weight: 20 lbs

Features	Output: Meter in % transmission; recorder, 0-10 mv, digital meter, 0-1 volt; slaved integrating digital voltmeter available	
Remarks	Aeration system and reagents required.[b]	
References	a) Manufacturer's brochure b) "Mercury in Water", EPA Storet No. Total 71900 (1974), Automatic and Manual Cold Vapor Techniques, Office of Technology Transfer, Washington, D.C. 20460	
Cost	Model HG-3	$2,495.00
Address	Spectro Products, Inc. 385 State Street North Haven, Connecticut 06473 (203) 281-0122	

E. SUMMARY AND RECOMMENDATIONS

Research needs for monitoring metals in water are generally in the areas of: (1) development of instrumentation with increased sensitivity and selectivity, (2) development of techniques for routine characterization and monitoring of individual forms of metals, (3) field evaluation of currently available monitoring methods; (4) development of reliable calibration techniques, (5) simplified laboratory procedures, and (6) development of continuous monitors.

Different forms of the same metal differ in their potential harm to man at equivalent concentration levels. For example, salts of trivalent chromium are not considered to be physiologically harmful, but hexavalent chromium in large doses can lead to corrosive effects in the intestinal tract. Possibly for this reason, 1962 drinking water standards limit hexavalent chromium levels to 0.05 mg/l but place no limitation on trivalent chromium. Headway is being made in differentiating chromium forms: a chemiluminescence method is sensitive only to trivalent chromium, and has a detection limit of about 0.025 ppb (Ref. 1). Hexavalent chromium can be measured without contribution from trivalent chromium to about 10 ppb using atomic absorption. In this method, Cr(VI) is extracted with ammonium pyrrolidine dithiocarbamate; Cr(III) is not extractable (Ref. 2, p. 105).

Aside from containing the element, soluble and insoluble forms of mercury differ in terms of source, effect, reactions, toxicology, and incidence of each metal species. Since the ability to study each species for these characteristics requires the availability of instruments for its detection and measurement, techniques for selective species analysis are needed. Not only must chemical forms be characterized, but also physical forms. Information such as the percentage of mercury or mercury compound adsorbed onto particulate matter and the quantity of insoluble mercury compounds in sediments would allow more accurate estimation of mobility, and need for cleanup.

Elemental mercury may be distinguished from nonvolatile combined mercury by sparging the element with a helium gas stream into a plasma excitation emission spectrophotometer (Ref. 3). The limit of detection is about 2 nanograms. Atomic absorption instruments are also capable of distinguishing elemental mercury from combined mercury. Gas chromatographic separation techniques have been applied to separate mercury compounds in solution. Dimethyl, diethyl, dipropyl, dibutyl, and methylmercury were determined using a six foot length column, with 5% DC-200, 3% QF-1 copacked on Gas Chrom Q; combustion of column effluent to form elemental mercury; followed by atomic absorption detection. Retention times were determined by calibration with known compounds. Concentrations as low as 0.001 μg/ml (ppm) dimethyl and 0.01 μg/ml of methylmercury were detected in water samples. Sumner and Saha applied the method of Westöö to isolate methylmercury as methylmercury chloride (Ref. 4). The methylmercury chloride was determined by electron capture gas chromatography using a five foot long, 1/8" diameter aluminum packed column with 10% carbowax 20 M or 80-100 mesh chromosorb W. The carrier gas was oxygen-free nitrogen; flow rate 60 ml/min; temperatures: injector 180°C, column 130°C, detector 200°C. Under these conditions, methylmercury chloride had a retention time of 4.5 minutes (Ref. 4).

Manufacturers of monitoring instrumentation for metals in water should review their equipment design at the earliest opportunity. Increased automation, sensitivity, selectivity, and the ability to substitute calibration standards for the water stream are of particular importance in new instrumentation. Increased sensitivity and selectivity in both field and laboratory instrumentation can decrease the number of pre-measurement steps required for an analysis. Procedures can be simplified and changes of sample loss or contamination minimized.

Atomic absorption spectrophotometers have virtually displaced molecular absorption (colorimetric) methods in laboratory analyses. Such metals as Cu, Fe, Mg, and Zn can be determined in fresh water by directly aspirating the aqueous solution into the flame. Total Cr, Mn, and Pb as well as Cu and Zn were determined directly by using more sensitive carbon rod or graphite atomizer techniques (Ref. 5). The graphite atomizer was applicable directly to the water sample; the flame method required solvent extraction preconcentration steps.

As ambient levels of metal pollutants decrease in compliance with legal requirements, it is desirable that monitoring instrumentation be able to cope with these lower levels. Recent methods with enhanced sensitivity include spark source mass spectrometry, plasma excitation emission spectrometry, differential pulse polarography and flameless atomic absorption. One might design specific field metal monitors by using atomic absorption graphite atomizer techniques to attain increased sensitivity. A Technicon or Hach stream sampler could be combined with the Perkin-Elmer or Varian Techtron instruments, and an automatic micropipetting arrangement. For multielement analyses, a stream sampler might be combined with a plasma excitation emission spectrometer so that simultaneous analysis is possible. Such instrumentation must be field tested to assess its reliability.

The instruments must be capable of accurate calibration either in the laboratory or in the field. Erroneous data are worse than no data at all.

Additional discussions of instrumentation needs in water quality measurements are included in the articles by Ballinger (Ref. 6, 7). and Stack (Ref. 8).

F. REFERENCES

1. W.R. Seitz, W.W. Suydam and D.M. Hercules, "Determination of Trace Amounts of Chromium (III) Using Chemiluminescence Analysis," Anal. Chem. 44 (6), 957 (1972).
2. Methods for Chemical Analysis of Water and Wastes, Environmental Protection Agency, Cincinnati, OH 45268 (1971).
3. R.W. April and D.N. Hume, "Environmental Mercury: Rapid Determination in Water at Nanogram Levels," Science 170, 849 (1970).
4. A.K. Sumner and J.G. Saha, "Methylmercury Concentrations in Muscle Tissues of Fish from the Saskatchewan River," Environmental Letters, 2 (3), 167 (1971).
5. S. Slavin, W.B. Barnett, H.L. Kahn, "The Determination of Atomic Absorption Detection Limits by Direct Measurement," At. Absorption Newslett., 11 (2), 37 (1972).
6. D.G. Ballinger, "Instruments for Water Quality Monitoring," Env. Sci. Tech. 6 (2), 130 (1972).
7. D.G. Ballinger, "Decisions to be Made in the Use of Automatic Water Quality Monitors," International Symposium on Identification and Measurement of Environmental Pollutants, Ottawa, Canada (June 14-17, 1971). EPA, AQCL, Cincinnati, OH 45168.
8. V.T. Stack, Jr., "Water Quality Surveillance," Anal. Chem. 44 (8), 32A (1972).

Halides & Cyanide
HAL

Nitrogen, Phos, Sulfur
NPS

NITROGEN, PHOSPHORUS AND SULFUR WATER MONITORING INSTRUMENTATION

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4. Control	
5. Effects	
6. National Water Quality Standards for NPS	
7. National Discharge Standards for NPS	
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3. Calibration	
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1.2 Gas Permeable Membrane Electrode	
1.3 Ion Selective Electrode	
1.4 Ultra Violet Absorption	
1.5 Charged Particle Activation Analyses	
2. Automated Laboratory Analyzers	
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D. Selective Methods and Instrumentation	H2O-NPS Sections
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F. References	
G. NPS-in-Water Instrument Notes	H2O-NPS Instrument Notes
1. Table of Instruments	

A. INTRODUCTION

This section discusses nitrogen, phosphorus, and sulfur (designated here as NPS) in fresh, waste, and saline waters, and particularly the effects of environmental factors on NPS monitoring. Topics covered include the sources, forms, and harmful effects of NPS in water, and a discussion on the natural cycling of NPS within the biosphere. These topics are discussed in detail in various publications (Ref. 1-5, 8,9).

The EPA has been promulgating new rules and regulations which set high standards for pollution including decreased effluent discharges from point sources. See Table A-1 for a listing of criteria for NPS for typical point source categories constructed from The Federal Register. A discussion is included in this section on methods for controlling NPS discharge which may be used to fulfill these regulations. A recent example of decreased pollutant discharges is that of ammonium nitrate (Ref. 13).

The brief discussion is also included on standards relevant to human health and welfare, and to national standards on the NPS content in drinking and other waters. Standards have been found necessary for both health and environmental reasons. Nitrate has been limited in drinking water due to the methemoglobinemia it can cause in infants. Nitrite is equally dangerous but occurs much less frequently at high concentrations. Discharges into waterways are limited in permissible nitrogen and phosphorous because of eutrophication of the receiving waters. Sulfur in the form of sulfide is of concern for health, environmental, and aesthetic reasons.

Apart from the effect of nitrate and nitrite on infants, and the laxative effect of high concentrations of sulfate, NPS limits in drinking water are of minor concern in most cases, phosphates even being added to water to control corrosion. NPS are of much more frequent concern in discharges into waterways, where the nutrient balance can be unfavorably affected by relatively small amounts of NPS in the discharges. Associated problems include harmful effects to aquatic animals, injurious effects related to the dyeing of wool and silk fabrics, harmful effects in fermentation processes, and increased corrosion. Some of these problems can be translated into an annual cost; for example, the cost for the restoration of eutrophic lakes, or the need to use excessive chlorine for purification of raw water containing a high NH_3-N content. Many problems are not as easily assessed, such as the cost for the loss of a recreational stream or lake. Some advances have been made in the reduction of NPS in man-related discharges, but much remains to be done.

Detailed reports and summaries of NPS in water are contained in various reports including in Water and Wastewater Engineering by Fair, Geyer, and Okun (Ref. 1), Water Quality Criteria by McKee and Wolf (Ref. 2), the EPA technology transfer document Process Design Manual for Phosphorus Removal by Black and Veatch (Ref. 3), the series of articles on the biosphere in Scientific American (Ref. 4), and the "Sources of Nitrogen and Phosphorous in Water Supplies: report by the American Water Works Association (AWWA) (Ref. 5).

1. Characteristics

Nitrogen, phosphorus and sulfur are common constituents of water which arise from both natural and man-released sources. Nitrogen and phosphorus are classified as nutrients because they are included among the elements essential to the growth of algae and other aquatic plants. The growth of algae in water requires a number of elements, but nitrogen and especially phosphorus are the ones most likely to be in limited supply in fresh waters. Many forms of NPS are found in fresh, saline, and waste waters, but only nitrate (NO_3-N) and sulfate (SO_4-S) are listed in the 1962 U.S. Public Health Drinking Water Standards. The 1975 Interim Drinking Water Standards list NO_3-N. This section will briefly summarize the characteristics of NPS.

Compounds of nitrogen and phosphorus are the primary nutrients that stimulate growths of algae and other plants and cause eutrophication of lakes and ponds. See Figure A-1. The following discussion is taken from Reference 1:

> *Eutrophication of the biosphere is the intensive cycling of phosphorus, nitrogen and sulfur. Curved arrow at bottom represents beginning of the process: the human use of phosphorus as fertilizer, which returns phosphorus to the lithosphere, thereby reversing the phosphorus cycle. Stright arrows at left and right indicate that phosphrous added to the lithosphere (and to phosphorus already present) is then taken up by phytoplankton and other organisms as well as by crops. Other straight arrows at right and left show that phosphorus and other elements return to the lithosphere and hydrosphere by decay. Once phosphorus is plentiful, scarcity of nitrogen and sulfur may limit eutrophication. Arrows at top represent carbon dioxide, nitrate and sulfate from industrial activity rising into atmosphere and falling in rain. They may promote eutrophication of dry land since vegetation may reabsorb them from air and*

TABLE A-1.
Typical Rules and Regulations on Point Source Discharges of NPS Pollutants.

Point Source Category	Pollutant	Maximum[a]	Average[b]	Reference
Steam Electric Power Cooling tower blowdown	Phosphorus	5.0 mg/ℓ	5.0 mg/ℓ	15
Electroplating (existing source)	Phosphorus	320 mg per m^2 per operation	160 mg/m^2 per operation	16
Electroplating (new source)	Phosphorous	160 mg/m^2 per operation	80 mg/m^2 per operation	17
Poultry Processing Products	Ammonia	8.0 mg/ℓ	4.0 mg/ℓ	18
Poultry Processing Products (new sources)	Ammonia	0.40 mg/k kg of LWK	0.20 mg/k kg of LWK	18
Inorganic Chemical Manufacturing	Ammonia	No discharge of process water to navigable waters		19
	Ammonia	8.8 kg/khg of product	4.4 kg/khg of product	19
Meat Products (Meat Cutter subcategory)	Ammonia (as N)	8.0 mg/ℓ	4.0 mg/ℓ	20
Fertilizer (Ammonium Sulfate subcategory)	Ammonia (as N)	30 mg/ℓ[c]		21
Meat Products and Rendering Processing	Ammonia	0.04 kg/hkg of raw material	0.02 kh/hkg of raw material	
Phosphate Manufacturing	Total Phosphorous	70 mg/ℓ	35 mg/ℓ	23
Glass Container Manufacturing (new sources)	Ammonia	104.0 g/hkg of product frosted	52.0 g/hkg of product frosted	24
Ferroalloys Manufacturing electrolytic manganese	Ammonia	40.667 hg/hkg of product	20.334 kg/hkg of product	25
electrolytic manganese dioxide	Ammonia	10.574 hg/hkg of product	5.287 hg/hkg of product	

[a] Maximum for any one day.

[b] Average of daily values for 30 consecutive days shall not exceed this number.

[c] Pretreatment Standard.

soil. Curved arrows indicate routes followed by elements that are both soluble and volatile.

The major drinking water quality problems that result from heavy algal growths are undesirable taste, odors, and filter clogging. In 1966, these problems were indicated to have affected as much as 56% of the total municipal surface water supplies in the United States. The important forms of nitrogen in water are ammonium-ammonia (NH_3-N), nitrite (NO_2-N), and nitrate (NO_3-N). These forms are water soluble and can be readily used for plant growth.

The elemental forms of NPS do not occur as such in water, and are of little or no importance in water quality monitoring. They are only briefly included in this discussion. A detailed treatment on the chemistry of nitrogen and phosphorus is contained in the Final Report of the Water Quality Division on Nutrients in Water, entitled "Chemistry of Nitrogen and Phosphorus in Water" (Ref.8).

Besides the natural cycling shown in Fig. A-1, NPS undergo a variety of chemical reactions, including complexation by metal ions, oxidation by dissolved oxygen, precipitation by cations such as iron and calcium. Gaseous forms of NPS (e.g. H_2S, NH_3) are removed to some extent in nature by volatilization, but environmental considerations make this an impractical treatment process in most cases.

The background concentrations of some forms of NPS in fresh waters is usually below $30\ \mu g/\ell$, except for sulfur, see Table A-2. Polluted waters, effluent discharges, estuarine water, and bottom sediments and sludges may have elevated levels of these pollutants.

2. Forms

The forms of NPS in water include both anions and cations, proteinaceous substances, dissolved gases, polymeric substances, in particles of detritus, in bottom sediments and in biological sludges. The NPS do not necessarily remain in their original form, but often are converted from one form to another depending on the conditions. For example, nitrogen originally discharged as ammonia is converted by oxidation into nitrite and eventually nitrate; a change in pH can convert sulfide

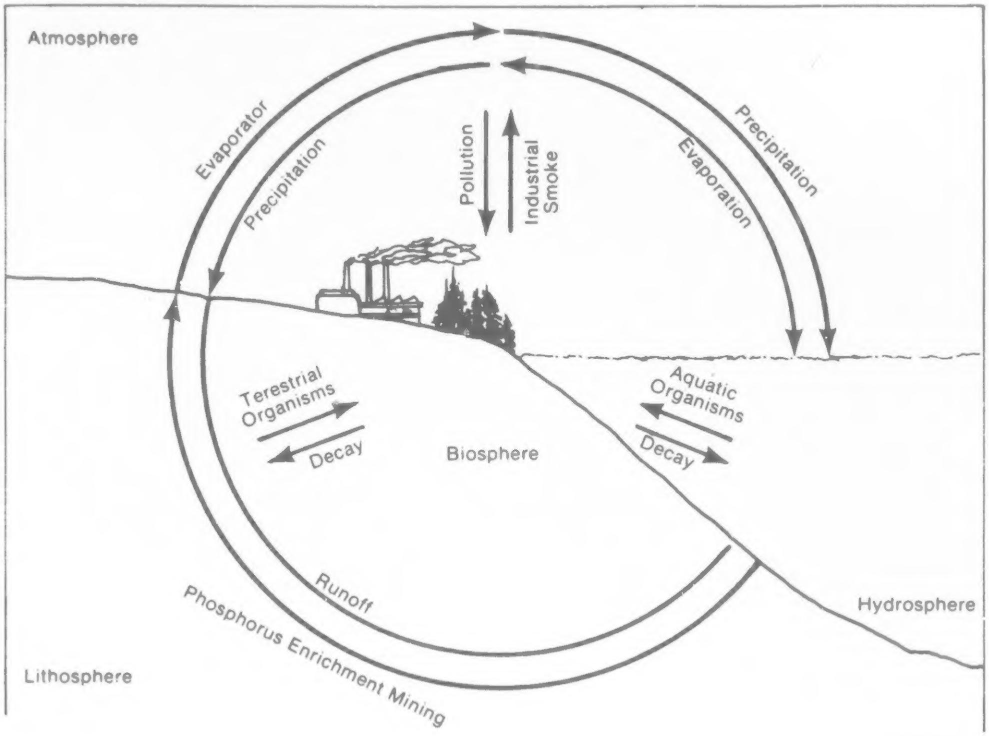

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Figure A-1. Eutrophication of the biosphere showing the cycling of phosphorus, nitrogen, and sulfur. (Ref. 4).

TABLE A-2.

Background Concentrations of Selected Forms of NPS in Fresh Waters

Element	Form	Amount	Reference
Nitrogen	NH_3-N	< 0.1 (as N)	12
	NO_3-N	< 10	11
	NO_2-N	< 0.1	11
Phosphorus		10-30 μg/ℓ	12
Sulfur	SO_4-S	median of 26 mg/ℓ	12

(HS^- or $S^=$) into gaseous hydrogen sulfide (H_2S); soluble phosphate can be converted into an insoluble phosphate by some metal cations. Water parameters which affect the form of NPS include pH, presence of oxidizing constituents such as dissolved chlorine and dissolved oxygen, and the presence of precipitating cations. Except for the refractory forms, virtually all forms of NPS are converted by bacterial action to other forms and are incorporated into algae and plants. The principal refractory form of phosphorus is that contained in soil, most of which is not immediately biologically available. Turbid runoff water from unoccupied watersheds may have total phosphorus values in excess of 1 mg/1. If impounded and allowed to settle, the overlying water may have filtrable phosphate values less than 0.01 mg/1. The amount of phosphate biologically available for eutrophication can not be judged from total phosphate values, although slow transformations and chemical equilibria can cause a release of phosphate from such refractory sources. Many data on phosphorus are impossible to interpret due to lack of knowledge of the form that was measured. Filtrable phosphate in raw water reservoirs is rarely of much significance since most of the phosphate is tied up in algae but is readily recycled.

From a monitoring standpoint, NPS pollutants are commonly analyzed, and results reported on the form which exists in the sampled water. For example, ammonia, nitrite, and nitrate are analyzed and measured as such.

3. Sources

Water supplies receive NPS in various forms from a large number of both natural and man-released sources including naturally occurring minerals, domestic waste waters, industrial effluent discharges, and water runoff from streets and agricultural land. Fresh and saline waters contain traces of phosphorus and sulfur which are leached or dissolved from naturally occurring minerals; waste waters contain nitrogen which primarily originates from feces, urine, and waste food (Ref. 5). Some forms of NPS may be greater than expected under certain conditions, for example sulfide may be found in distribution systems as a result of bacterial action on organic matter under anaerobic conditions (Ref. 11).

There has been an increase in the domestic supply of NPS. For example, over the five year time span 1970-1974, the domestic supply of phosphorus increased from 3,171,000 tons to 5,359,000 tons, nitrogen increased from 3,982,000 tons to 9,969,000 tons (Ref. 6). In 1973, the U.S. consumed 10,250,000 long tons of sulfur (all forms), and an estimated 10,955,000 long tons in 1974 (Ref. 7).

In a study of street surface contaminations, the EPA estimated streets contained weighted means of 1.1 lb/curb mile phosphates and 0.094 lb/curb mile nitrates (Ref. 26). These street contaminants (as well as other pollutants) have been found to contribute substantially to urban pollution when washed into receiving waters by storm runoff.

The reader is referred also to Table A-1 which lists typical manufacturing point sources for ammonia and phosphorus pollutants. Besides the references to The Federal Register given in this table, Standard Methods, 14th edition, contains information on natural man-released sources of NPS pollutants.

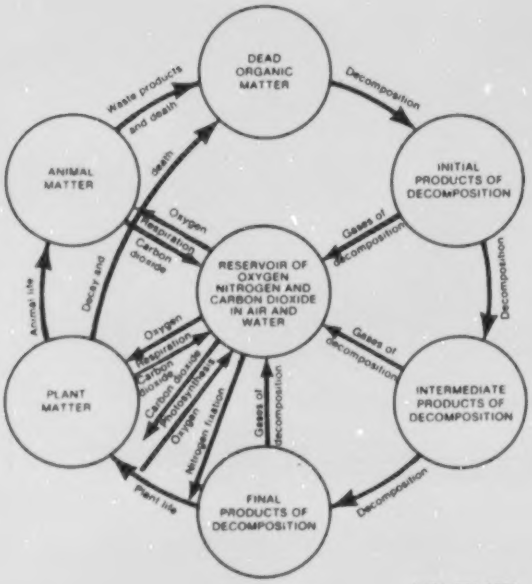
4. Control

Methods of controlling the NPS content of water discharges include natural purification, removal by chemical or physical means, and by biological treatment. An example of natural purification is the oxidation of sulfite to sulfate by dissolved oxygen. The rate of natural purification by a stream depends on many factors, for example pH, temperature, concentrations of other water constituents, and the extent to which the receiving stream previously has become acclimated to such pollutants. For sulfite, the reaction velocity coefficient ranges from 0.236 per day to 0.412 per day, where the rate of oxidation follows a first-order law (Ref. 2).

Man-operated controls for NPS commonly use biochemical processes to remove NPS. For example, municipal sewage treatment depends upon the establishment of a complicated mixed culture of microorganisms that is acclimatized to the particular type of waste. This culture then uses the dissolved and suspended organics in the waste as an energy and carbon source. The biological solids are then separated from liquid wastes which are subsequently discharged either to the environment or to additional treatment. Nitrates and phosphates are added if the waters being treated are deficient in either of these essential minerals.

Some wastewater effluents, even though they have been biologically treated, may still contain substantial amounts of phosphates. Under these conditions phosphates are removed from the effluents by chemical precipitation using multivalent metal ions, such as ferric alum or calcium (Ref. 1, p. 29-32 and p.34-5). Hydrogen sulfide is removed from water by aeration techniques.

Oxygen is needed both for the microorganisms in the aerobic decomposition of organic matter and for the plants and animals that resynthesize organic matter. Gaseous oxygen supplies the normal dissolved oxygen requirements in water: about 0.8% by volume at normal temperatures (50°F) as compared to 21% by volume in the atmosphere. In the absence of dissolved oxygen, anaerobic bacteria utilize the oxygen contained in NO_3-N, PO_4-P, SO_4-S. The cyclic anaerobic transformations of nitrogen, sulfur, and phosphorus are shown schematically in Fig. A-2. Carbon dioxide and methane are the most common gases released; they escape to the atmosphere after the waters become saturated (Ref. 1).


DEAD ORGANIC MATTER
Decomposition
INITIAL PRODUCTS OF DECOMPOSITION
Decomposition
INTERMEDIATE PRODUCTS OF DECOMPOSITION
Decomposition
FINAL PRODUCTS OF DECOMPOSITION
Plant life
PLANT MATTER
Animal life
ANIMAL MATTER
Waste products and death
Decay and death
RESERVOIR OF OXYGEN NITROGEN AND CARBON DIOXIDE IN AIR AND WATER
Oxygen
Respiration
Carbon dioxide
Oxygen
Respiration
Carbon dioxide
Carbon dioxide
Photosynthesis
Oxygen
Nitrogen fixation
Gases of decomposition
Gases of decomposition
Gases of decomposition

(XBL 771-132)

Figure A-2. Cycles of carbon, nitrogen, and sulfur in anaerobic decomposition. (Ref. 1).

Some of these control processes simply replace one form of an NPS pollutant by another; so that the overall approach must be examined to evaluate fully the various options. For example biochemical oxidation of the nutrient ammonia yields nitrate, which is also an algae and plant nutrient.

In the case of ammonium nitrate, ion exchange techniques were used in a recent application. The wastewater was contacted with a strong acid cation exchange resin that removed the ammonium contaminant and reduced its level to less than 3 mg/1. The decationated water was then contacted with a weak base resin in the hydroxide form that reduced the nitrate content to 7-100 mg/1 NO_3-N (Ref. 13).

5. Effects

The harmful effects of NPS to man and aquatic biota depend on such factors as the form, concentration, and water pH. For example, the toxicity of ammonia and ammonium salts to fish is directly related to the concentration of undissociated ammonium hydroxide in the water. This, in turn, is a function of the pH of the water. See McKee and Wolf (Ref.2).

Specific effects on man and fish differ for the various forms of NPS, and are discussed in the individual sections for nitrogen, phosphorus, and sulfur.

6. National Water Quality Standards for NPS

The U. S. Public Health Service has published guidelines for drinking water which include recommended limits for nitrate, sulfate, and a threshhold odor number. These guidelines have been periodically reissued over the past fifty years to reflect changes in recommended limits. The drinking water standards have been revised four times; a summary of the last revision (1962) is given in Introduction to this volume. The EPA issued interim drinking water standards in March 1975 which are expected to form the basis for the National Standards. See Appendix III.

Similar guidelines also are available for water used for recreation; fish and wildlife, agricultural uses; and various industries. Information may be obtained from the Introduction to this volume, McKee and Wolf (Ref. 2), and Water Quality Criteria, 1972 (Ref. 12).

7. National Discharge Standards for NPS

Point source effluent discharge standards related to the discharge of nitrogen, phosphorus, or sulfur into waters are currently being promulgated. There are many such standards, and the reader should consult The Federal Register for the appropriate point source classification. See Table A-1.

B. MONITORING SYSTEMS

The number of steps or modules required for measuring NPS contents in water depends to a large extent on both the interferences and concentration of NPS. For example, turbidimetric analysis can be applied directly to fresh water samples for SO_4-S, and the gas permeable electrode can be applied to measure NH_3-N in fresh, waste, and saline waters. Other methods may require pre-measurement steps to separate NPS from interferences, or to enhance the concentration of NPS. Ion-exchange, distillation, filtration and precipitation methods are among these pre-measurement steps.

The different forms of NPS usually are converted by chemical reactions into a single form, which is subsequently measured. Thus, evaluation of methods for monitoring to determine their reliability must include the entire system and not just the instrumental measurement.

Although the actual instrumental measurement is central to the analytical procedure, it is only one portion of an overall water monitoring system. The integrity of the analysis performed by a complete monitoring system depends on a number of factors including sampling site selection, pollutant sampling and preservation procedures, pollutant chemical or physical separation methods, completeness of any required chemical reactions, sensor operation and signal quantification, data processing, and calibration. Each of these steps is of importance, so that the entire monitoring system must be fully understood to assess the reliability of the data. Erroneous data are frequently worse than no data at all.

Water quality measuring systems can be classified for use in either fresh, waste, or saline waters. Freshwater systems are those designed for natural (unpolluted) and treated waters. They are used for a reconnaissance of the Nation's resources, and to establish background levels for water constituents. Wastewater monitoring systems are those suitable for analyzing the discharges from point sources such as industrial or municipal effluents. They may require filtration of the sample to remove floating particles and other debris that would interfere with subsequent steps of analysis. Saline water systems are used to measure pollutants in estuarine waters or brines. They may require special features as means of compensation for the high mineral content of the sample.

The complete system for monitoring water quality must be evaluated for reliability, durability, ruggedness, and cost. The integrity of the processed data requires accuracy when compared with known standards, specificity in the presence of interfering constituents, sensitivity for the pollutant being determined, and repeatability in terms of repetitive measurements by one laboratory as well as reproducibility among many testing laboratories. To allow intercomparison of data, one needs also to record the temperature, depth, flow rate, and direction of the water stream being sampled. These data permit assessment of mass concentration, mass flow, and water composition.

1. Systems Concept

Systems for monitoring NPS in water can be classified as either manual or automated analyzers. In addition, they may be of the laboratory or field type.

Laboratory manual NPS monitoring systems involve sampling on-site grab samples followed by analysis in the laboratory. Manual implies human involvement in all stages of analysis except the actual instrumental measurement. Samples for NPS analysis usually are collected in a bottle fabricated from polyethylene or a similar material to minimize adsorption or leaching contaminants from the sides of the container. A preservative technique (e.g., addition of zinc solution, storage at 4°C) is often used for the sample.

Laboratory automated NPS systems involve sampling on-site, followed by anlysis in the laboratory. One or more of the following steps are then performed automatically, sample uptake, reagent mixing, color development, and sometimes instrumental readout. As in laboratory manual systems, samples are contained usually in plastic bottles to which a preservative is added. Field manual analyzers are portable, and contain any needed chemical reagents in kits. Any necessary measuring instruments are usually battery powered. Analyses are performed on grab samples at the site; preservatives are not required to minimize losses of NPS.

Field automated monitoring systems are of the type in which a sample stream is separated from the water and analyzed on-site with an automatic analyzer. Data may be continuous or periodic.

When data taking is not interrupted it is defined as being continuous. If data are recorded only periodically, a sampling process takes place, and the information is called sampled data. For example, an uninterrupted chart record of NH_3-N is continuous, a reading every hour is sampled.

2. Sampling

Sample collection and preparation are complicated for NPS in water because of such factors as the low concentrations, frequent necessity of sampling from a moving stream, interferences, diversity of soluble forms and the presence of NPS in the particulate state and in sediments. Samples taken for laboratory analysis are collected in a polyethylene or glass bottle to which preservatives have been added. See Table B-1 (Ref. 27). The added preservatives guard against losses of NPS. For example, added H_2SO_4 converts gaseous NH_3 to the nonvolatile NH_4^+; added Zn acetate converts gaseous H_2S to insoluble ZnS (zinc sulfide). The pollutants are regenerated by adding NaOH, thus converting NH_4^+ back to NH_3; and H_2SO_4 to convert ZnS to H_2S.

TABLE B-1.

EPA Recommended Grab Sample Containers, Preservatives, and Holding Periods for NPS Pollutants (from Ref. 27)

Pollutant	Preservative	Holding Period (Days)
NO_3-N	pH < 2 with H_2SO_4; 4° C	1
NO_2-N	4° C	1
NH_3-N	pH < 2 with H_2SO_4; 4° C	1
Kjeldahl-N	pH < 2 with H_2SO_4; 4° C	1
PO_4-P	Filter at site; 4 C	1
Total Dissolved-P	Filter at site; 4° C	1
H_2S-S	2 ml Zn acetate	1
SO_3-S	4° C	1
SO_4-S	4° C	7

Either plastic or glass containers are satisfactory sample containers.

The necessity for sample preservation is indicated by the study on the kinetics of oxidation of sulfide in water by dissolved oxygen as a function of pH (Ref. 32). As shown in Fig. B-1, the specific rates of sulfide disappearance go through maxima at pH 8 and pH 11, and a minimum at pH 9. The solubility of H_2S and NH_3 in water decreases with increasing temperature; low temperatures for storing samples are required to prevent significant losses due to temperature fluctuations.

Sample concentration methods include precipitation of H_2S-S as ZnS and increasing the sample size from 500 to 1000 ml for NH_3-N.

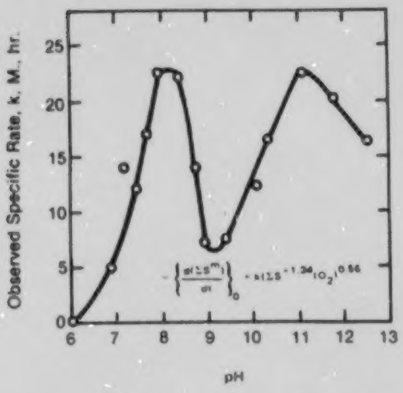


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Figure B-1. pH dependence of observed specific rate of sulfide oxidation (see Table II for details) (Ref. 32).

Interferences are minimized by using a number of methods including the following: distillation (e.g. NH_3-N), stripping with an inert gas, (e.g., H_2S-S); and background correction (e.g., PO_4-P).

When a NPS pollutant exists in samples in several different forms, sequential analyses of the same form may be used. For example, if NO_2-N is determined, NO_3-N may then be reduced to NO_2-N, another nitrite determination made, and the NO_3-N calculated by difference. Similarly, after the determination of PO_4-P (filtrable), organic phosphorus may be oxidized to PO_4-P which is determined, and the organic phosphorus calculated by difference. Polyphosphates may be hydrolyzed to PO_4-P and calculated in the same manner, in the absence of organic phosphates. Such techniques must be used with care to avoid compounding errors, since the treatment necessary to release one form may also affect another form.

Tradeoff considerations related to different sampling procedures for laboratory and field monitoring systems include: (1) the laboratory sample usually is at a low temperature and may contain acid added as a preservative; the field sample may not, (2) the time lapse between sampling and analysis is longer for laboratory monitoring. A significant time lapse may be undesirable. For example, real-time information is necessary for water quality surveillance within a time frame which encompasses the instant of undesirable occurrence through an ensuing period of time when successful correction is practical (Ref. 33).

Sampling may also be automatic. Once set up, the automatic sampler does not require human assistance other than periodic checking. See Figure B-2 for a schematic of a typical commercially available automatic sampler (Ref. 29). In this example, water being sampled

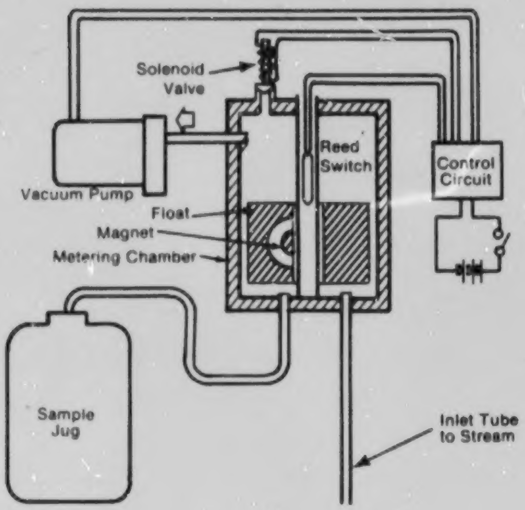

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Figure B-2. Typical automatic sampler (from Ref. 29).

is pumped into the metering chamber and causes the float to rise. When a pre-determined volume of water has entered the chamber, the magnet closes the reed switch to activate the solenoid valve. Activation of the solenoid stops pumping and permits the sampled water to flow both into the sample jug and, in a rinsing action, back through the inlet tube.

Additional information on NPS sampling is contained in Standard Methods, 14th ed. (Ref. 28). The U.S. Geological Survey Book 5 entitled Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases contains a detailed description of both sampling and manual samplers (Ref. 30). About 40 commercially available automatic sewer flow samplers are described in the EPA report on An Assessment of Automatic Sewer Flow Samplers (Ref. 31).

3. Calibration

Calibration can be one of two kinds: instrument and systems. Instrument calibration methods include impression of a known electrical signal at the inputs of the instrument, use of an optical filter, or introduction of a known concentration of NPS through a portion of the monitoring system. The true concentration of NPS in water samples cannot be calculated if only the instrument is calibrated because NPS may be gained or lost in untested portions of the monitoring system. Calibration of the entire monitoring system is best accomplished by introducing known concentrations of NPS directly at the sampling stage.

Calibration methods generally include the categories: (1) calibration curves and (2) standard additions.

A calibration curve is obtained by analyzing known concentrations of the NPS in exactly the same way that the samples will be analyzed. Use of the identical, or a similar sample, to minimize matrix effects is important. The instrumental readout is corrected for the blank and plotted versus known NPS concentration to obtain the calibration curve. Changes in room temperature, instrumental blank, or reagent purity affect this curve.

In the method of standard addition, small volumes (often several microliters) of a solution containing a known concentration of NPS are added to the sample prior to analysis. Any necessary volume correction is made to take into account dilution caused by addition of the standard, and the instrument readout is calculated for both the known and unknown NPS concentrations. The fraction of the signal output related to the known concentration of the added NPS is determined and the concentration of the NPS in the sample is calculated. The method depends on a linear relationship between concentration and signal output; a blank correction for background must be made. Two or more standard additions should be carried out to obtain reliable results.

TABLE B-2
Ortho- and Total Phosphate in River Water Before and After Addition of Orthophosphate

	Mg/ℓ.ortho P			Mg/ℓ.total P		
Sample	Before	Added	After	Before	Added	After
1	0.05	0.25	0.29	0.07	0.25	0.32
2	0.05	0.25	0.25	0.06	0.25	0.28
3	0.32	0.25	0.56	0.42	0.25	0.68
4	0.15	0.20	0.32	0.20	0.20	0.40
5	0.29	0.20	0.45	0.33	0.20	0.45

Average % recovery of added orthophosphate:
ortho P = 95.0, total P = 97.0.

Table B-2 shows calibration data for PO_4-P in river water samples using the method of standard additions. The monitoring system used was a Technicon Auto Analyzer with automated sample-reagent mixing, and colorimetric intensity readout on a strip-chart recorder. A solution of disodium hydrogen phosphate (Na_2HPO_4) was used as the calibration standard. The solution was prepared by drying 4.759 g of solid Na_2HPO_4 for 1 hour at 105°C; this was dissolved in 1000 ml. of distilled water containing 10 ml. of 37% formaldehyde solution. The final solution had a concentration of 1000 mg/1 PO_4-P (Ref. 34).

Table B-3 shows calibration data for NH_3-N for both standard additions and a calibration curve (direct measurement). (Reference 35). As shown, both methods gave comparable results. The method of standard additions is preferred because matrix effects (e.g., temperature changes, differences in ionic strength, etc.) are better compensated. The NH_3-N standard was prepared from solid NH_4Cl. This NH_4Cl was first dried at 100°C for 3 hours; then 3.819 g. were dissolved in 1000 ml of Super Q water to give a final concentration of 1000 mg/1 NH_3-N. This standard solution was stable for at least one month.

TABLE B-3
Direct Measurement and Known Addition
Comparison (Ref. 35).

Sample	Direct measurement, mg NH_3-N/ℓ	Known addition, mg NH_3-N/ℓ	Difference	
			mg NH_3-N/ℓ	%
A	0.367	0.376	+0.009	+2.5
B	0.146	0.145	-0.001	-0.7
C	0.198	0.201	+0.003	+1.5
D	0.168	0.167	-0.001	-0.6
E	0.137	0.134	-0.003	-2.2
F	0.122	0.118	-0.004	-3.3
G	0.112	0.114	+0.002	+1.6
H	0.026	0.032	+0.006	+23.0
I	0.191	0.198	+0.007	+3.7

Calibration standards for NPS monitoring systems are available from a very large number of laboratory supply houses. Analytical Chemistry published a laboratory guide in August 1974 which listed a number of these supply houses.

Caution is required in the use of standard methods because of the multiplicity of forms which may be present and not all of which may respond to the analytical method. Properly chosen pre-treatment is essential in such cases.

Additional information on NPS calibration is obtained from Standard Methods, 14th Ed. (Ref. 28), and the EPA Methods Manual (Ref. 27).

4. Units

NPS are commonly reported as mg/l (milligrams per liter) or µg/l (micrograms per liter).

C. NPS IN WATER INSTRUMENTATION

Prior to about 1940, NPS pollutants were analyzed by using volumetric and gravimetric procedures. These methods still form the basis for many standard methods used today. Since then, however, instrumental methods have achieved greater prominence because of increased sensitivity, selectivity, amenability of automation, and eventual lower cost per sample due to a decrease in turnaround time.

Instrumentation for monitoring NPS in water can be classified in a number of ways. It is convenient to separate it as follows: manually operated laboratory analyzers, automated laboratory instrumentation, manual field monitors, and automatic field monitors. Table C-1 lists the four classes of instrumental techniques commonly used for measuring NPS in fresh, waste, or saline water.

Well-designed automated laboratory instrumentation can perform mechanical operations more rapidly and with more precision than can an operator with the equivalent manual means; also, the results obtained have a higher repeatability than manual laboratory methods. For example, the EPA has found that automated instruments such as the Technicon AutoAnalyzer permit 20 to 60 NH_3-N determinations per hour without requiring operator attention. However, these automated analyzers have the disadvantage that a given manifold arrangement can cover only a limited concentration range, making the instrument incapable of compensating for an unusual sample condition (for example, unexpectedly high concentration). The setup time required to perform a given analysis is fairly long so that automation is worthwhile only when a large number of samples are to be examined.

1. Manual Laboratory Analyzers

Manual operation implies human involvement to progress along the various steps in an analytical procedure. Despite significant advances in instrument automation, most NPS water monitoring information is still obtained with manually operated laboratory analyzers. This is due in part to cost considerations in comparing manual and automated equipment, as well as the lengthy time involved in accepting new procedures as standard methods.

1.1. Colorimetry

Colorimetric methods (ultraviolet-visible absorption spectrophotometry) generally involve forming a colored species by means of chemical reactions between a reagent and the NPS pollutant under analysis. Polychromatic light from a source such as a tungsten lamp is passed through a monochromator, which directs a narrow bandwidth of the incident light through a cell containing the absorbing species. The attenuation in light intensity owing to absorption is corrected for background ef-

TABLE C-1
Commonly Used Instrumental Methods for NPS in Water Measurements

Instrumental Method	Pollutant Measured
Manual laboratory analyzers	
Colorimetric	NH_3-N, NO_2-N, NO_3-N; SO_4-S, H_2S-S, PO_4-P
Turbidimetric	SO_4-S
Gas Membrane Electrode	NH_3-N; NO_2-N
Ultraviolet Spectrophotometry	NO_3-N
Charged Particle Activation Analysis	NO_3-N
Ion Selective Electrode	NO_3-N
Automated laboratory analyzers	
Colorimetric	NH_3N, NO_2-N, NO_3-N
Manual field monitors	
Colorimetric	NH_3-N, NO_3-N; PO_4-P, H_2S-S
Volumetric Titration	SO_4-S; SO_3-S
Automated field monitors	
Colorimetric	PO_4-P; NH_3-N
Gas Membrane Electrode	NH_3-N

fects and related to concentration of NPS in the water sample through calibration data. Optimum results may depend on several factors, including the following: adjustment of oxidation state, maintenance of the correct pH, removal of interferences, and solvent extraction. Samples should be measured within a specified time period after the color-forming reaction to minimize problems of color fading.

Colorimetric methods lack specificity and sensitivity, and are time consuming. To obtain suitable specificity distillation or precipitation techniques are commonly used.

Attractive features of colorimetric techniques for water analysis include the relatively low costs (less than $1000 for some instruments), portability, and the known reliability of the analytical methods.

The schematic of the essential parts of a typical colorimeter is shown in Fig. C-1. See the specific sections on NPS monitoring analyzers for typical analytical procedures, and the H2O-MET Section for a discussion of colorimeters. Additional discussions are found in Standard Methods, 14th Ed., the ASTM Book, Part 31 (Ref. 36), and the EPA methods manual, and Instrumental Methods of Analysis, 5th Ed. (Ref. 37).

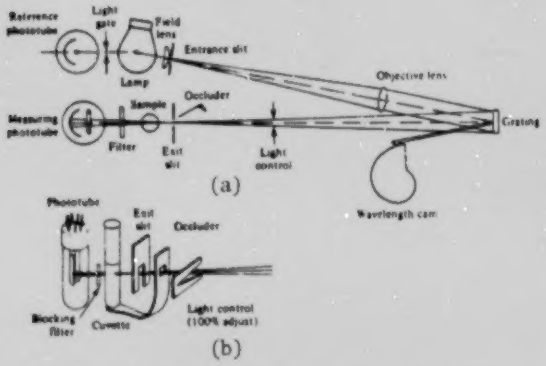


Figure C-1. Bausch & Lomb Spectronic 20 colorimeter. (a) Schematic optical diagram. (b) Detail of photocell.

Turbidimetric methods are principally used to monitor SO_4-S using either light scattering or light transmission measurements. See H2O-PHY, Turbidity. A potential source of error here is the effect of dissolved (or true) color. This effect is compensated for by measuring the sample before the addition of $BaCl_2$ reagent to establish a background level.

1.2. Gas Permeable Membrane Electrode

In gas permeable membrane electrode analyzers, the gaseous pollutant dissolved in water diffuses through a semi-permeable membrane (e.g., Teflon) into an electrochemical cell compartment. The electro-chemical cell compartment contains a sensing electrode, a reference electrode, and a supporting electrolyte such as ammonium chloride or potassium hydroxide. The semi-permeable membrane serves a dual function: it separates the electrochemical cell from the water sample, and it permits primarily only the dissolved gas being monitored to diffuse from the water sample through the membrane into the supporting electrolyte. The dissolved gas may subsequently react at the sensing electrode, and thus cause an electrical current. The dissolved oxygen electrode (DO probe) is an example of this kind of electrode. Alternatively, the gas may change the acidity of the supporting electrolyte, and thus cause a change in the measured pH. The ammonia electrode functions in this manner. See Figure C-2 (Ref. 37).

The ammonia electrode is not affected by other dissolved gases in the water sample unless these gases both diffuse through the membrane, and have an acidic or basic nature (for example, CO_2, H_2S) when dissolved in ammonium chloride. When measuring total ammonia at high pH, CO_2 and H_2S do not interfere because they are present as $CO_3^=$ or $S^=$ ions and are no longer in the gaseous form.

In water solutions containing ammonia, the following chemical equilibrium holds:

$$NH_4^+ + OH^- \rightleftharpoons NH_{3(gas)} + H_2O. \qquad (1)$$

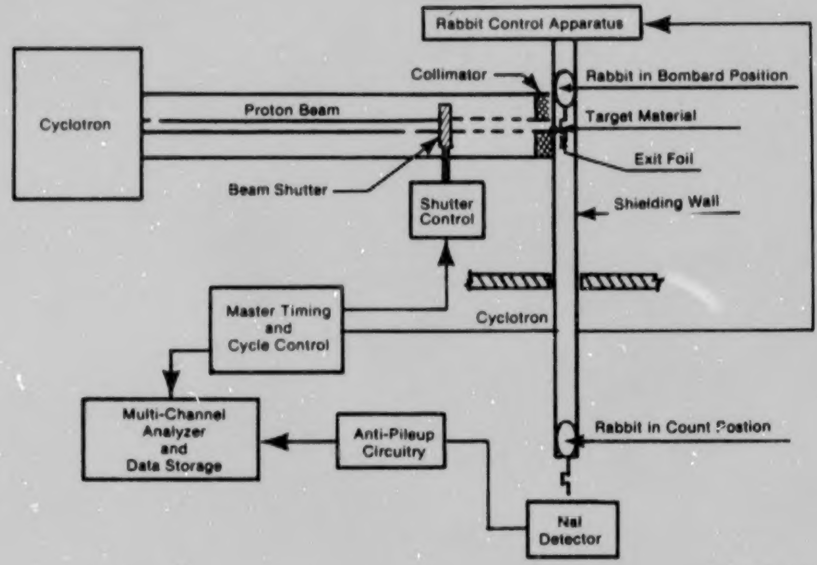
At high pH values (e.g., pH 11), the equilbrium shifts to the right, and gaseous ammonia is freed from the ammonium ion (NH_4^+); it may subsequently diffuse through the membrane. The water sample is normally adjusted to pH 11 by addition of small amounts (e.g., 1 ml) of 10 N NaOH; equation (1) is thus shifted far to the right. The NH_3 which permeates the membrane then dissolves in the ammonium chloride filling solution where the reverse of equation (1) takes place:

$$NH_{3(gas)} + H_2O \rightleftharpoons NH_4^+ + OH^-. \qquad (2)$$

The increase in OH^- causes a rise in pH which is detected by a mirror flat glass electrode. The glass electrode responds to changes in the NH_3 concentration in the filling solution according to the Nernst equation:

$$E = E_x - S \log[NH_3]. \qquad (3)$$

Here, E is the potential of the NH_3 electrode, E_x is a constant, and S is the electrode slope which is approximately 50 mV per decade at 29°C. The reference electrode is a chloride ion-selective electrode; its potential remains fixed because the chloride concentration in the supporting electrolyte is fixed. Changes in the output voltage of the ammonia sensor are thus


Rabbit Control Apparatus
Cyclotron
Collimator
Rabbit in Bombard Position
Proton Beam
Target Material
Exit Foil
Beam Shutter
Shutter Control
Shielding Wall
Master Timing and Cycle Control
Cyclotron
Multi-Channel Analyzer and Data Storage
Anti-Pileup Circuitry
Rabbit in Count Position
NaI Detector

(XBL 771-131)

Figure C-2. Activation analysis techniques (Ref. 37).

due to changes in the pH-sensitive glass electrode and are related to NH_3 concentration in the water sample by calibration data.

The EPA has studied the application of the NH_3 gas membrane electrode (Ref. 2) to water monitoring. As a calibration standard, analytical reagent grade NH_4Cl is dried at 100°C for 3 hours; 3.819 gm (1000 mg/1 NH_3-N) are then dissolved in 1.0 liter of Super Q water which has been passed through a Millipore Super Q water purification system containing a prefilter, a carbon filter, a mixed-bed ion exchange column, and an 0.2 μ filter. The calibration standards prepared from the NH_4Cl and the Super Q treated water are stable for at least one month.

To test this standard, an Orion Model 95-10 NH_3 electrode was used as the sensor; readings were obtained on an Orion Model 801 digital pH meter, coupled to a Model 851 digital printer. To obtain readings, a 70-ml volume of the calibration standard was made basic by adding one ml of 10 N NaOH, and stirring with a magnetic stirrer. The electrode sensor was inserted immediately, and a reading taken after 5 min equilibration time. Calibration data covering the range 0.03 to 2.0 mg NH_3-N/1 are shown in Table C-1. The direct measurement calibration curve gave results comparable to the standard additions method. See Table C-2.

Interferences in the operation of the Orion 95-10 NH_3 electrode include volatile amines such as methyl amine or ethyl amine which diffuse through the membrane and cause a change in the pH of the electrolyte. Organic solvents and wetting agents may shorten the membrane electrode life. The temperature of measurements should be closely controlled, because there is a 1% change in apparent NH_3 concentration per °C.

TABLE C-2
Ammonia Concentration vs.
Electrode Potential at 25°C (from Ref. 35).

Concn. of Standard, mg NH_3-N/1	Absolute Potential, mV	Concn. Measured, mg NH_3-N/1
2.0	-21.0	2.06
1.0	- 3.3	1.00
0.5	14.3	0.49
0.2	38.3	0.19
0.1	53.8	0.099
0.05	69.1	0.053
0.03	83.4	0.029

The standard additions method has the advantage that changes in both temperature or ionic strength are more readily compensated for than with the direct method. However, any volume changes must be calculated for the known volume of added standard solution: the final NH_3 concentration must be on the linear portion of the calibration curve so that the concentration of NH_3-N in the water sample can be calculated by interpolation.

The selective ion method using gas permeable electrodes is listed in the EPA Methods Manual of December 1974 (Ref. 27). Both the Orion Model 95-10 and the EIL Model 8002-2 electrodes are listed in the apparatus section. Caution should be taken to ensure that the pH is 11 or above; otherwise freeing NH_3 from NH_4^+ ion will be incomplete.

1.3 Ion-Selective Electrode

Ion selective electrodes respond to the change in activity of the ionic species being measured in a water sample, but are not specific for that ion. The first highly selective electrode was the glass electrode which is used for pH measurement. Changes in the composition of the glass membrane in the construction of these electrodes permits enhanced response to ions such as NH_4^+.

The response of an ion selective electrode to several ionic species may be represented by the Nernst equation written in the following form:

$$E = E^\circ - \frac{RT}{NF} \ln(A + K_b B + K_c C)$$

where the K's represent the various selectivity ratios, plus the electrode response of any interfering ion relative to the response of the ion being measured. A,B, and C represent the activities of the NH_4^+ and interfering ions. Manufacturer's brochures often list the values of K for a given electrode, and these may be used to estimate the range of usefulness of an electrode in a given analytical situation.

For example, the Beckman ion-selective electrode 39137 responds to K, NH_4, Na, and Li ions (in descending order of sensitivity).

The NH_4^+ electrode was used to develop a rapid method for determining NH_4^+ in water when concentrations are greater than 0.5 mg/l. Neither dilution nor pretreatment of the water sample is required. The accuracy of the NH_4^+ electrode for application to boiler feed water from power stations was investigated. The electrode response time varied from two minutes for concentrations at the 1000 mg/l level, to 8 minutes for the 10 mg/l concentration (Ref. 38).

1.4. Ultra Violet Absorption

The ultraviolet method is a spectrophotometric technique used for NO_3-N which depends on the attenuation of light at 220 nm and 275 nm. The method differs from colorimetric methods in that chemical reactions to form a colored solution are not required because NO_3-N absorbs near-UV radiation.

1.5. Charged Particle Activation Analysis

Charged particle (nuclear) activation analysis is an activation method in which neutrons are replaced by other nuclear particles. See H2O-MET for a discussion of neutron activation analysis. The schematic for laboratory instrumentation is shown in Figure C-3. The method was applied to nitrogen (NO_3-N) in fresh water, samples at the μg/l level (Ref. 39).

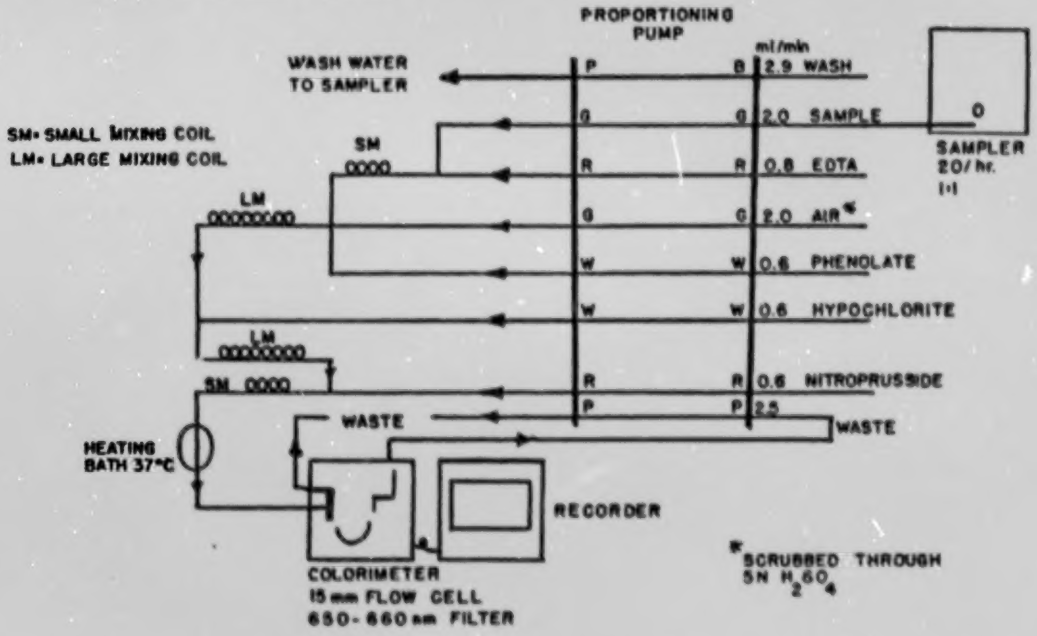
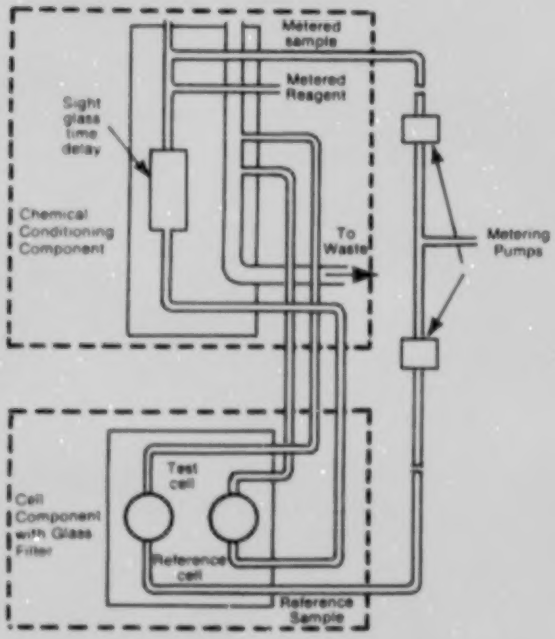

PROPORTIONING PUMP
ml/min
WASH WATER TO SAMPLER
SM= SMALL MIXING COIL
LM= LARGE MIXING COIL
SM
LM
LM
SM
P
G
R
G
W
W
R
P
B 2.9 WASH
G 2.0 SAMPLE
R 0.8 EDTA
G 2.0 AIR*
W 0.6 PHENOLATE
W 0.6 HYPOCHLORITE
R 0.6 NITROPRUSSIDE
P 2.5
WASTE
WASTE
SAMPLER 20/hr. 1:1
HEATING BATH 37°C
RECORDER
COLORIMETER 15 mm FLOW CELL 650-660 nm FILTER
*SCRUBBED THROUGH 5N H_2SO_4

Figure C-3. Ammonia manifold AA1 (Ref. 39).

2. Automated Laboratory Analyzers

Automated laboratory instrumentation includes NPS systems in which one of the following functions do not require human intervention: (1) insertion of the sample into the colorimeter sample changer. An example is the Gilford 2443-A rapid sampler in which the cuvette remains in the measuring beam for both filling and purging. About 0.7 ml of the sample is drawn into the cuvette by means of a vacuum, and returned to the sample container by application of pressure. The sampler can process about 300 samples per hour; (2) Recording of concentration readings. The Varian Techtron Model 36 digital printer is an example of automated data recording: recordings are at a maximum rate of one line every two seconds, and results falling outside a pre-selected concentration range are tagged by asterisks.
(3) Central measuring analyzers with attached modules in which required chemical reactions are automatically performed in chambers to which samples and reagents are pumped and mixed. The Technicon AutoAnalyzer is an example of this category of automated laboratory instrumentation. This system automatically performs the following functions: sampling, filtering, diluting, reagent addition, mixing, heating, digesting, color development, and measurement of the color produced. See Fig. C-4 (Ref. 27).



(XBL 771-134)

Figure C-4. Delta 8000 automated field monitor. (Ref. 27).

For example, the EPA includes a method of determining ammonia colorimetrically by using the AutoAnalyzer. The instrument train includes the following: sampler; manifold proportioning pump; heating bath with double delay coil; a colorimeter equipped with 15-mm tubular flow cell and 630- or 650-nm filters; and a recorder. The basic chemical reaction between ammonia nitrogen and sodium phenolate solution in the presence of sodium hypochlorite forms a blue-colored reaction product. The concentration of ammonia is related to the intensity of the blue color by calibration data.

See the specific NPS section for application of laboratory automated instrumentation.

3. Manual Field Monitors

These monitors are portable kits and instruments that measure pollutants by a variety of methods including volumetric titration and colorimetric reactions. In the latter case, the intensity of the color is determined by comparison with liquid-in-glass color standards, or a reagent-impregnated paper. For titration, a color change signals the end-point in the titration. The LaMotte Octet Comparator outfits are examples of the liquid-in-glass comparator measurements. Another approach to colorimetric intensity determination is that used by the Bausch and Lomb MiniSpec 20 battery-powered spectrophotometer. This instrument measures the attenuation in light intensity from a sample, and relates the reading to the pollutant concentration by calibration data.

The Delta Scientific Series 260 is a portable (weighs about 5 kg) colorimeter powered by two 6 volt batteries for field use. Readout is by means of an analog meter scale. It has a listed sensitivity of 0.05 mg/l NH_3-N; 1.0 mg/l H_2S-S; 0.15 mg/l NO_3-N; 0.0006 mg/l NO_2-N; 0.01 mg/l PO_4-P; 1.0 mg/l SO_4-S; and 0.6 mg/l SO_3-S.

Manual field monitors contain reagents and necessary glassware for use in on-site measurements using standard procedures. They have the advantage that sample losses (e.g., H_2S_1 NH_3) are minimized, and preservatives may not be required. Caution is necessary to be certain the instrument is properly calibrated, that reagents have not deteriorated, and that glassware is free from contaminants.

4. Automated Field Monitors

Automated field monitors can be classified as either continuous or semicontinuous samplers. Continuous sampler instruments measure a constituent on an uninterrupted basis, and include both probe-type continuous samplers (such as NH_3 electrode) and wet chemical analyzers (such as Delta Model 8000 analyzer). The Enviro Control Series 2000 wet chemical analyzer is an example of a semicontinuous sampler. A metered sample from the water stream is filtered and mixed with a fixed quantity of reagent. Depending on the rapidity of the chemical reaction between reagent and water constituent, the sample of water and reagent is passed either through a delay coil to allow time for color development, or directly into a colorimeter. The colorimeter contains a single lamp source and two matched cells. The colored sample stream passes through one cell, while the unreacted water stream passes through the other. The difference in light intensity is detected and recorded as a measure of the pollutant concentration.

Additional information on automated field monitors is obtained from Ballinger (Ref. 41), Stack (Ref. 42), and Ciaccio (Ref. 43).

5. Summary and Recommendations

Research needs for monitoring NPS in water are generally in the areas of: (1) increased selectivity, (2) development of methods for routine characterization and monitoring of individual forms of NPS, (3) development of reliable calibration techniques, especially for the field monitors, (4) simplified laboratory procedures, (5) development of point-source discharge monitors.

Monitoring NPS is hampered by the dependence on colorimetric measurements. These require the addition of color-forming reagents, and time for the color to develop. Turbidity, dissolved color, and other water constituents may interfere and must be compensated for, e.g., by filtration or distillation. Automated laboratory and field analyzers such as the Technicon and Orion monitors assist in removing some of the tedium of analyzing a large number of samples. The reliability of data gathered using automated field monitors depends on frequent calibration of the entire monitoring system.

The reader is referred to the sections on Nitrogen, Phosphorus, and Sulfur which follow this general introduction for a further discussion on recommendations for NPS monitoring system.

TABLE C-3
Direction Measurement and Known Addition Comparison (from Ref. 35).

Sample	Direct Measurement, mg NH_3-N/1	Known Addition, mg NH_3-N/1	Difference	
			mg NH_3-N/1	%
A	0.367	0.376	+0.009	+ 2.5
B	0.146	0.145	-0.001	- 0.7
C	0.198	0.201	+0.003	+ 1.5
D	0.168	0.167	-0.001	- 0.6
E	0.137	0.134	-0.003	- 2.2
F	0.122	0.118	-0.004	- 3.3
G	0.112	0.114	+0.002	+ 1.6
H	0.026	0.032	+0.006	+23.0
I	0.191	0.198	+0.007	+ 3.7

D. SELECTIVE NPS METHODS AND INSTRUMENTATION

This section surveys the literature on instrumental methods which are or might be applied to monitoring NPS in water. The literature coverage is selective; the intent is to give examples of both current and developing methods.

1. Nitrogen in Water

This section is limited to the NH_3-N, NO_2-N and NO_3-N forms of nitrogen.

Ammonia

a. Colorimetric

The primary limitations of colorimetry for analyzing nitrogen in water are interferences due to water constituents (e.g., turbidity) and the length of time required for analysis. For example, measuring the NH_3-N content in fresh waters by the Nessler method requires preliminary distillation of ammonia from sample buffered at pH 7.4. The distillation reduces interferences due to turbidity, dissolved color, alkalinity or acidity. Close control of pH is required to minimize conversion of organic compounds to NH_3-N, and to optimize the recovery of NH_3-N. The USGS method for distilling ammonia is similar to that in Standard Methods, 14 Ed., except that it follows the EPA procedure in adjusting to pH 9.5 with borate buffer. The water sample is adjusted to pH 9.5 using a borate buffer to decrease hydrolysis of any cyanate in organic nitrogen compounds. The released NH_3 is then distilled into a solution of boric acid (Ref. 3).

Following distillation, a portion of the distillate is Nesslerized. Essentially, Nesslerization is the reaction between potassium mercuric iodide ($HgI_2 \cdot 2KI$) and ammonia to form a red-brown complex of mercuric ammonobasic iodide, according to the following equation:

$$HgI_2 \cdot 2KI + NH_3 \rightarrow Hg(NH_2)I + 2KI + HI.$$

The concentrations of ammonia are then determined by standard UV-VIS spectrophotometric measurements. Alternatively, NH_3 in the distillate may be titrated with a standard sulfuric acid solution (Ref. 8).

Interferences include a number of aromatic and aliphatic amines, and any compounds which cause turbidity upon the addition of Nessler reagent. Direct Nesslerization of the water sample (i.e., without distillation) cannot be used because of the many interferences. For example, cyanate (CNO^-), will hydrolyze to some extent even at pH 9.5; volatile alkaline compounds such as hydrazine will interfere with the titrametric results. Residual chlorine must be removed by pretreatment of the sample with sodium thiosulfate before distillation, and if the sample has been preserved with a mercury salt (e.g., $HgCl_2$), the mercury ion must be complexed with sodium thiosulfate prior to distillation. The Nessler method is sensitive to 20 µg/l NH_3-N under optimum conditions. Optimum results are obtained over the range 0.05 to 1.0 mg/l for the colorimetric procedures, and from 1.0 to 25 mg/l for the titrimetric procedure.

The precision and accuracy of the method given in the EPA manual was tested by 24 analysts in 16 laboratories using water samples containing concentrations of ammonia covering the range 0.21 to 1.92 mg/l. See Table D-1 (Ref. 14). Additional information on the precision and accuracy of this method for determining ammonia nitrogen is found in Standard Methods (Ref. 11).

Besides Nesslerization, Standard Methods lists a tentative phenate method for the colorimetric determination of ammonia. The method

TABLE D-1
Twenty-four Analysts in Sixteen Laboratories Analyzed Natural Water Samples Containing Exact Increments of an Ammonium Salt, With the Following Results (from Ref. 14).

Increment as Nitrogen, Ammonia (mg N/liter)	Precision as Standard Deviation (mg N/liter)	Accuracy as	
		Bias, %	Bias, ng N/liter
0.21	0.122	- 5.54	- 0.01
0.26	0.070	-18.12	- 0.05
1.71	0.244	+ 0.46	+ 0.01
1.92	0.279	- 2.01	- 0.04

utilizes the reaction of ammonia, hydrochlorite and phenol, catalyzed by manganous salt to form the intensely blue indophenol. Interferences in the method include: > 500 mg/1 alkalinity, > 100 mg/1 acidity, or any dissolved color or turbidity. These interferences may be removed by preliminary distillation. For information on the precision and accuracy of this method, see Ref. 5.

Automated laboratory colorimetric methods of analysis for NH_3-N in water usually employ the Technicon instrument system. The EPA is very active in developing automated methods for water monitoring, and lists an automated method for monitoring ammonia based on the indophenol blue color formed by the reaction of ammonia with alkaline phenol hypochlorite. The method is applicable to the determination of NH_3-N present in either surface or saline waters. Concentrations in the range 0.01 to 2.0 mg/1 NH_3-N may be determined, depending upon the selection of the size of the flow cell and the extent of dilution of the sample. See Figure D-1 (Ref. 44).

Calcium and magnesium ions cause precipitation during the analysis; adding a 5% solution of EDTA eliminates the source of error. Other sources of error include variations in the acidity or alkalinity of the water sample, due to the pH dependence in the intensity of the color which is measured. The pH of washwater and the standard ammonium solution should approximate that of the sample to avoid causing a pH change. Added $HgCl_2$ causes a negative interference because mercury complexes with ammonia. This complex may be compensated for by adding an equivalent amount of $HgCl_2$ to the ammonia standards which are used for the preparation of the standardization curve. As an additional precaution, when saline water samples are analyzed, substitute ocean water (SOW) should be used for preparing the ammonia standards used for the calibration curve.

The precision and accuracy of the method were tested by EPA's Analytical Quality Control Laboratory using surface water samples containing 1.41, 0.77, 0.59 and 0.43 mg/1 NH_3-N. The standard deviation was ± 0.005.

The Technicon AutoAnalyzer was also applied to the measurement of NH_3-N in sanitary and storm sewer waters in the Minneapolis--St. Paul sanitary district (Ref. 45). Besides ammonia, other measured parameters were COD, methylene blue-active substances, chlorides, Fe, PO_4-P, urea, and total (Kjeldahl nitrogen). The alkaline phenol method was used for NH_3-N; calibration solutions were prepared by dissolving 1.146 g/ℓ of NH_4Cl, (300 mg/1 NH_3-N) in a stock solution which also contained 20,000 mg/1 COD, 5000 mg/1 cl. 500 mg/1 PO_4-P, and 1000 mg/1 urea. The stock solution was diluted for calibration purposes.

The method of standard additions was applied for recovery studies. See Table D-2. The developed automated method was compared with the manual method for NH_3-N. See Table D-3.

Brinkmann Instruments has recently introduced a probe colorimeter that can be used to monitor NH_3-N. The probe is inserted directly into the test solution, which may be in a beaker or a test tube. The probe is

TABLE D-2
Recovery of Standards Mixed with Primary Effluent

		Prim.Eff. + Standard		% Recovery		
Analysis	Prim.Eff. mg/liter	Actual mg/liter	Theor. mg/liter	Min.	Max.	Avg.
NH_3-N	6.8		[illegible].4	101.0	105.4	102.1
COD	293	543	546	95.8	105.1	99.4
Cl	80	142	140	100.7	103.0	101.5
PO_4	11.2	15.3	15.6	94.6	102.6	98.1
Urea	6.7	27.0	23.4	103.0	134.9	115.3
Fe	0.41	0.37	1.20	16.7	40.0	30.8
*Kjeldahl N	18.9	19.2	19.5	91.0	106.0	98.1

*4 days only.

TABLE D-3
Automated vs. Manual Ammonia
Determinations

	Average NH_3-N-mg/liter				
			% of Manual		
	Manual	Auto.	Min.	Max.	Avg.
Raw	11.0	10.7	94.1	100.0	97.1
P.E.	11.2	11.3	98.4	103.9	101.2
S.E.	9.7	9.3	95.5	96.2	95.9

based on transmitting phase-shifted light through a fiber optic light guide to the probe tip. The probe tip is made of stainless steel and has both a glass window and an aluminized glass plate or convex lens held in place. Light passes through the sample to the mirror, and back through the sample again to the fiber optics. After passing through the sample, the light is passed through a filter and then to a photometric cell which converts the light intensity to an electrical signal read on a scale.

The probe colorimeter light is AC amplified and phase-shifted to minimize effects of the ambient light, thus permitting colorimetric measurements when the sample is in an open container. For the indophenol method, the range is 0.01 to 2.0 mg/1 of NH_3-N measured at 650 nm (Ref. 46).

Colorimetric methods are used in manual field analyzers. For example, the Hach DR/2 colorimeter is battery-powered for field use, and weighs about 6.5 kg. It covers the wavelength range of 400 to 700 nm, and has the following listed ranges for nitrogen in water analysis using standardized methods: o to mg/1 NH_3-N, 0 to 30 mg/1 NO_2-N, 0 to 0.2 mg/1 or o to 150 mg/1 NO_2=N. The optical light path is shown in Fig. D-1.

The Ecologic Instrument Corp. Series 500 instruments are examples of automated field analyzers. The monitors utilize wet chemical methods for color development, and utilize modified standard procedures. For example, NH_3-N is monitored by the phenol-hypochlorite method in which the blue color intensity is measured at 650 nm. The reagents required for color development are contained within the instrument, and are metered to a mixing coil using a peristaltic pump. The sample flow rate is 200 ml/hr.; the time required for a 90% response is about 15 minutes.

In summary, colorimetric methods are those most widely used for monitoring NH_3-N in the field and in the laboratory. Laboratory methods have the disadvantages of requiring sample preservation to minimize NH_3-N loss, and of having a time delay between sampling and analysis. Field analyzers can provide real-time data and may not require sample preservatives. However, unless NH_3-N is separated from the sample by distillation, the analyses are subject to interferences which require compensation. Automated methods provide the capability of analyzing a large number of samples relatively inexpensively and appear desirable.

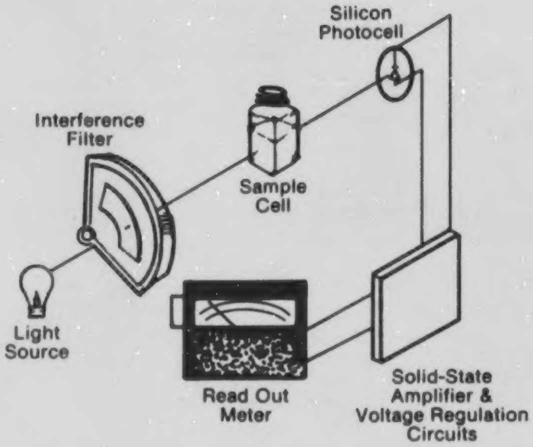


Figure D-1. Light path diagram.

b. Gas Membrane Electrodes

The laboratory analysis of NH_3-N using gas membrane electrodes is listed in the EPA Methods manual for fresh, saline, and waste water samples (Ref. 44). The method covers the range 0.03 to 1400 mg/1 NH_3-N; Color and turbidity do not interfere, and prior distillation is unnecessary. The samples are preserved for 24 hours by refrigeration at 4°C, or, for longer periods, by addition of H_2SO_4 to pH <2 (2 ml conc H_2SO_4 per liter of sample) for longer holding periods. Mercuric chloride forms strong complexes with NH_3-N; this complexed NH_3-N is not measured by the electrode so that $Hg Cl_2$ cannot be used as a preservative.

The distilled water used to prepare reagents must be free of NH_3-N; this is accomplished by passing the water through a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin. In analysis, 100-ml of the water sample are placed in a 150-ml beaker, an electrode such as the Orion Model 95-10 or EIL Model 8002-2 is inserted, 1-ml of 10 N NaOH is added, and the solution stirred while reading the meter. The final pH must be above 11. The meter reading is related to NH_3-N concentration by calibration data. The EPA found the following precision: using surface water samples of 1.00, 0.77, 0.19 and 0.13 mg/l NH_3-N, standard deviations were ±0.038, ±0.017, *0.007, and ±0.003, respectively.

The method has been applied to various waste waters. See Tables D-4, D-5, and D-6 (Ref. 47).

TABLE D-4
(Ref. 47) Comparison of Ammonia-Specific Ion Electrode With Standard Procedure for Petroleum Refinery Effluents

Laboratory reference number	Sample description	Ammonia N µg/ml, ammonia-specific ion electrode	Ammonia N µg/ml, distillation and acid titration	Ammonia N µg/ml, distillation and nesslerization
T-1111	Petroleum refinery A, effluent A (treated)	12.7		13.2
T-1112	Same as above	11.3		12.6
T-1113	Same as above	11.0		11.2
T-1114	Same as above	10.8		10.5
T-1115	Same as above	12.6		11.5
T-1118	Same as above	19.5		19.0
T-1219	Same as above	20.5	24.2	
T-1220	Same as above	11.8	9.9	
T-1222	Same as above	33.0	30.3	
T-1228	Same as above	10.0	10.5	
T-1296	Petroleum refinery B, effluent B (treated)	12.0	11.2	
T-1297	Same as above	13.0	13.3	
T-1298	Same as above	17.3	17.0	
T-1299	Same as above	19.3	20.4	
T-1300	Same as above	16.2	17.6	
T-1301	Same as above	15.8	15.4	
T-1302	Same as above	15.0	16.5	

TABLE D-5
(Ref. 47) Comparison of Ammonia-Specific Ion Electrode with Standard Procedure for Various Waste Waters

Laboratory reference number	Sample description	Ammonia N µg/ml, ammonia-specific ion electrode	Ammonia N µg/ml, distillation and acid titration	Ammonia N µg/ml, distillation and nesslerization
T-1156	Food processing plant effluent (untreated	108	101	99
T-1159	Food processing plant effluent (treated)	15.1	13.3	
TWB-1	Municipal sewage effluent (untreated)	5.4	5.6	5.6
TWB-2	Municipal sewage effluent (treated)	4.2	5.2	4.8
T-1231	Acid and explosive plant effluent (untreated)	99	92	
T-1232	Same as above	104	96	
T-1233	Same as above	2.4	3.0	
T-1234	Same as above	5.3	5.1	
TWB-10	Pulp and paper, sulfite mill effluent (untreated)	1300	1340	
TWB-11	Pulp and paper, kraft mill effluent (untreated)	3.2	34.6	39.0
TWB-12	Pulp and paper, kraft mill effluent (treated)	2.2	4.1	3.4
T-456	Chemical plant (detergent) effluent B (treated)	11.0	10.4	12.4
T-458	Chemical plant (detergent) effluent A (treated)	3.2	3.1	3.6
T-460	Chemical plant (detergent) effluent (untreated)	0.3	< 0.5	0.4

TABLE D-6
(Ref. 47) Comparison of Ammonia-Specific Ion Electrode with Distilled and Nondistilled Waste Waters

Laboratory reference number	Sample description	Ammonia N μg/ml, ammonia-specific ion electrode		Ammonia N μg/ml, distillation	
		Direct reading	Distillate	Nesslerization	Acid titration
TWB-1	Municipal sewage effluent (untreated)	5.4	6.1	5.6	5.6
TWB-2	Municipal sewage effluent (treated)	4.2	4.5	4.8	4.2
TWB-11	Pulp and paper, kraft mill effluent (untreated)	3.2	34.0	39.0	34.6
TWB-12	Pulp and paper, kraft mill effluent (treated)	2.2	3.6	3.4	4.1
T-1156	Food processing plant effluent (treated)	108	102	99	101
T-1220	Petroleum refinery A effluent (treated)	9.9	12.3		11.8
T-1222	Same as above	28.5	30.0		30.3
T-1228	Same as above	10.0	11.3		10.5
T-456	Chemical plant (detergent) effluent B (treated)	11.0	11.9	12.4	10.4
T-458	Chemical plant (detergent) effluent A (untreated)	3.2	3.5	3.6	3.1
T-460	Chemical plant (detergent) effluent (untreated)	0.3	0.4	0.4	< 0.5

Orion Research has recently introduced its Model 1110 automated field NH_3-N monitor. The standard range is 1.0 to 100 mg/l, with a lower limit of detection of 0.17 mg/l. See Fig. D-2. It requires 8 minutes for a 99% response to a change in NH_3-N concentration at the inlet. The sampled water stream is filtered prior to reagent mixing and measurement. (Ref. 48).

Enviro Control Inc. has available its Model 1057 NH_3-N gas membrane automated field monitor which is applicable to wastewaters. It covers the range 0.017 to 17,000 mg/l. The Model 1057 is combined with the Model 2052 or 2050 filtration unit which removes particles to 0.45 μ or 5μ, and the Model 1035 pH adjusting system. Total NH_3-N is measured by raising the pH, thereby converting NH_4^+ ions to dissolved NH_3 gas.

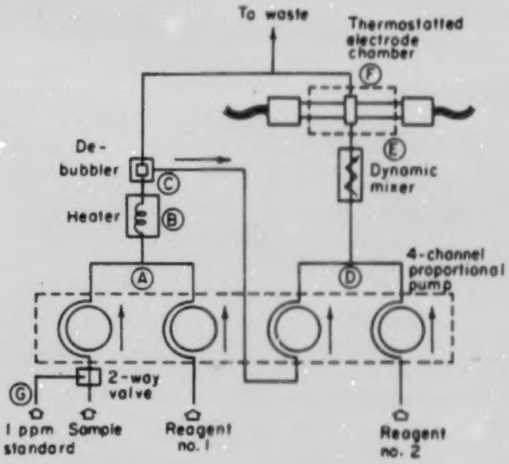


Figure D-2. Schematic of the Orion Research Model 1110 NH_3-N monitor (from Ref. 48).

In summary, the gas membrane method is utilized for measuring NH_3-N in waters; prior distillation is not required, and color and turbidity do not interfere. The method is promising for monitoring NH_3-N using laboratory or field methods. Caution must be exercised in choice of preservative, maintaining the required high pH and following the analytical procedure closely. The field automated monitors should be evaluated for application to specific joint source discharges.

Nitrate

Standard Methods, 14th Ed. and the EPA manual list colorimetric methods for NO_3-N; Standard Methods also includes a tentative UV absorption method.

a. Colorimetric

Colorimetric methods are most commonly used for analyzing NO_3-N in fresh, waste and saline waters. In fresh waters the phenol disulfonic acid method is listed in Standard Methods, while the brucine, cadmium and zinc reduction methods, as well as the chromotropic acid method, are equally satisfactory. In waste waters, it is more difficult to determine NO_3-N than in fresh waters because of high concentrations of numerous interfering substances (e.g., chlorides, organic matter). Consequently, several tentative methods are given in Standard Methods. The EPA methods manual and the USGS manual both list the brucine method: NO_3-N and brucine react in acid medium to produce a yellow color whose intensity is a function of NO_3-N concentration. Close attention must be given to procedural techniques if accuracy and precision are to be obtained.

b. UV Absorption

Standard Methods also lists a tentative ultraviolet (UV) spectrophotometric method for measuring nitrate. Measurement of the nitrate concentration using the ultraviolet method is made at a wavelength of 220 nm. The nitrate calibration curve follows Beers Law up to 11 mg/1 nitrogen. To correct for any absorption effects caused by dissolved organic matter which also absorbs at 220 nm, a second measurement is made at 275 nm, where nitrate does not absorb. The correction for dissolved organic matter absorption is then made by subtracting the absorption at 275 nm from that at 220 nm. Besides dissolved organic matter, nitrite, hexavalent chromium and surfactants also interfere with the UV method. Sulfate, NH_4^+ · HCO_3^-, PO_4-P, and F^- have negligible interference at the concentrations normally present in drinking water. The minimum detectable concentration for NO_3-N using UV absorption is 40 μg/1.

In the brucine method for NO_3-N, organic color, NO_2-N, and strongly oxidizing or reducing agents interfere. The interferences are removed; for example, residual chlorine up to 5 mg/1 is eliminated by addition of sodium arsenite; interferences of NO_2-N to 1 mg/1 are eliminated by addition of sulfanilic acid. Brucine is reacted with NO_3-N in 13 N H_2SO_4 solution at a temperature of 100°C to form a yellow color which is measured at 410 nm. Temperature control of the color reaction is extremely critical. The absorbance of the nitrate-brucine solutions was investigated as a function of color development time over a nitrate range of 0 to 100 mg/1 and over a time interval of 5 to 35 min (Ref. 8). It was found that the absorption curve did not flatten out at the point of 1:1 stoichiometry between brucine and nitrate, but instead dropped to absorption levels within the rnage of the 0.1 - 2 mg/1 of NO_3-N standard curve before increasing again. See Fig. D-3. Results of the experiment showed that without a stoichiometric equivalent or excess of brucine over nitrate, the brucine method can lead to erroneous results. (Ref. 49).

The EPA methods manual lists the automated determination of nitrogen in either the NO_3-N or the NO_2-N form; the initial step involves reducing nitrate to nitrite using a cadmium-copper catalyst. The nitrites, those originally present, as well as any nitrate that has been reduced to nitrite, are then reacted with sulfanilamide to form a diazo compound. This is coupled in an acid solution at pH 2.0 - 2.5 with N-1-naphthylethylenediamine hydrochloride to form the azo dye. The azo dye color intensity is proportional to the nitrite concentration and is measured using a UV-VIS spectrophotometer.

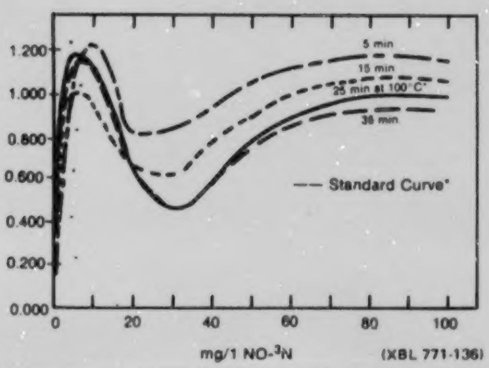


Figure D-3. Absorbance vs. NO_3-N concentration as a function of color development time (from Ref. 49).

Interferences are caused by the presence of ammonia and primary amines which are frequently present in natural waters and react to some extent with nitrites to form nitrogen. In the surface waters normally analyzed, the concentration of oxidizing or reducing agents and potentially interfering metal ions are well below the limits causing interferences with this method. When present in sufficient concentration, metal ions may produce a positive error; for example, Hg and Cu ions form complex ions having absorption bands at 543 nm where the colorimetric measurements are made. (Ref. 44).

The precision and accuracy of the automated method for nitrate-nitrite determination using cadmium reduction was assessed by three laboratories which analyzed four natural water samples containing exact increments of NO_3-N. See Table D-7.

TABLE D-7
Comparison of Precision Accuracy of Automated Methods for Nitrate-Nitrite (Ref. 14)

Increment as Nitrate Nitrogen (mg N/liter)	Precision as Standard Deviation (mg N/liter)	Accuracy as Bias, %	Accuracy as Bias, mg N/liter
0.29	0.012	+ 5.75	+0.017
0.35	0.092	+18.10	+0.063
2.31	0.318	+ 4.47	+0.103
2.48	0.176	- 2.69	-0.067

c. Charged Particle Activation Analysis

Charged particle activation analysis differs from neutron activation in that particles other than neutrons (e.g., protons, deuterons) are used in nuclear reactions. For example, the following reactions were used for analysis of nitrogen in water:

$$^{14}N + p \rightarrow {}^{14}O + n$$

$$^{14}O \rightarrow {}^{14}N + r + e^{+} + v.$$

These reactions were used to analyze NO_3-N in fresh water detritus (Ref. 50). A 4-ml. water sample was evaporated in a 5mm diameter, 1 mm deep indentation in a 1.59 cm diameter tantalum foil of 0.006 mm thickness. The Ta foils were irradiated with an 8 MeV beam of protons generated from a 76 cm cyclotron for 60 sec. After a 30 sec. wait, the gamma emission was counted using a NaI (Tl) crystal mounted on a photomultiplier tube. The limit of detection was about 20 μg/l. Silver nitrate was used for calibration.

Water samples from a number of sources were measured. The results shown in Table D-8 correlated well with chemical analysis for NO_3-N, indicating nitrogen was principally present as nitrate in these waters.

TABLE D-8
Results of Application of Nitrogen-activation Method to Various Water Sources. (Ref.21).

Sample Origin	Date	ppb
1. Lake Tahoe, California; supplied Dept. of Zoology, Univ. of Calif., Davis	March, 1972	21 ± 16
2. Tapwater, Environmental Eng. Lab., Univ. of Calif., Davis	6/14/71	45 ± 31
3. Drinking water, Walker Hall, Univ. of Calif., Davis	6/14/71 7/ 4/72	80 ± 32 340 ± 110
4. City of Davis, California	6/ 7/72	755 ± 35
Well Number 10	6/ 7/72	180 ± 45
Well Number 17	6/ 7/72	2835 ± 266
Well Number 18		
5. Sacramento River, Three-Mile Slough	April, 1972	83 ± 43
6. Colorado River, below Lake Havasu	3/23/71	400 ± 80

Nitrite

a. Gas Permeable Membrane Electrode

Orion Research model 95-46 electrode measures NO_2-N dissolved in water. (Ref. 51). Nitrite is measured by acidifying the water sample to convert nitrite to nitrous acid according to the reaction

$$NO_2^- + H^+ \quad HNO_2 \rightleftharpoons NO_2 + NO.$$

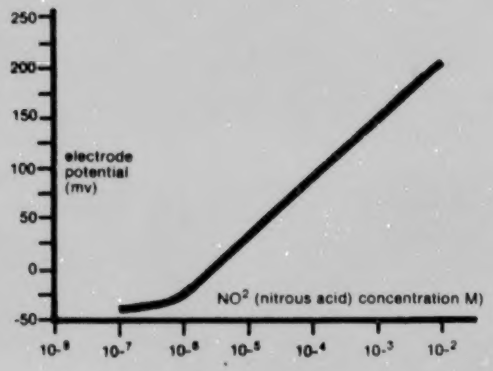
The dissolved HNO_2 then is in equilibrium with NO_2 and NO. The NO_2 diffuses through a highly gas-permeable membrane to a filling solution until equilibrium is reached between the HNO_2 level in the sample and the internal filling solution (electrolyte) of the electrode. Hydrogen ions are formed in the internal filling solution by the dissociation of HNO_2 according to the reaction

$$HNO_2 \rightarrow H^+ + NO_2^- .$$

The hydrogen ion level of the internal filling solution is measured by the internal sensing element and is directly proportional to the level of HNO_2 in the water sample. The electrode potential is essentially Nernstian:

$$E = E_x + n\log[HNO_2] .$$

See Fig. D-4. Nitrite in sewage effluents and industrial waste waters can be measured to 0.02 mg/l, with the upper limit 460 mg/l NO_2-N. Sample must be adjusted to pH 1.7 prior to analysis. The time response of the electrode



(XBL 771-135)

Figure D-4. Typical response of the model 95-46 nitrogen oxide electrode (from Ref. 51).

in going from dilution solutions to more concentrated solutions is 3 - 4 minutes. The maximum allowable concentration of interfering gases in 10^{-4} M HNO_2 solution is acetic acid, 3×10^{-3}; formic acid, 2×10^{-4}; HCl, > 1 molar.

b. Colorimetric

Standard Methods, the EPA methods manual, and USGS all list the diazotization method for analyzing nitrite in water. Nitrite is diazotized with sulfanilamide and the resulting diazo compound is coupled with N-(1-Naphthyl)-ethylenediamine dihydrochloride to form an intensely colored red dye. The intensity of the color measured at 540 nm is proportional to the nitrite concentration. The method is applicable in the range 0.05 - 1.0 mg/l NO_2-N. There are very few known interferences at concentrations less than 1000 times that of nitrite. However, addition of strong oxidants or reductants to the samples will readily affect the nitrite concentrations. High alkalinity, greater than 600 mg/l, will give low results due to a shift in pH of the color reaction which should occur between 1.5 - 2.0. A synthetic unknown sample contining 250 μg/l NO_2-N, 108 mg/l Ca, 82 mg/l Mg, 3.1 mg/l K, 19.9 mg/ Na, 241 mg/l Cl, 1.1 mg/l NO_3-N, 259 mg/l SO_4-S, and 42.5 mg/l total alkalinity was determined by the diazotization method. The relative standard deviation was 21.4% and the relative error was 12.0% in 49 laboratories.

The automated method for NO_3-N listed in the EPA methods manual can be applied to the determination of NO_2-N. (Ref. 44).

2. Phosphorus in Water

This section is limited to orthophosphate (PO_4-P) because it is the most prevalent form of phosphorus in water, and because other forms are usually converted to PO_4-P prior to analysis. Two methods commonly used are discussed: manual UV-VIS (colorimetry), and automated methods.

Orthophosphate

a. Manual UV-VIS Absorption Spectrophotometry

Standard Methods, 14th Edition, lists three methods for PO_4-P: (1) vanadomolybdophosphoric, (2) stannous chloride reductant method, (3) ascorbic acid reductant method (Ref. 52). See Table D-9. The method determines PO_4-P, so that other forms of phosphorus must be converted to phosphate by chemical means (e.g., oxidation) prior to analysis.

In the vanadomolybdophosphoric method, a water sample containing 50 - 1000 μg PO_4-P

TABLE D-9
Manual UV-Visible Absorption Spectrophotometric Methods. (Ref. 52)

Method	Ortho-phosphorus Phosphate μg/l	No. of Laboratories	Relative Standard Deviation %	Relative Error %	Minimum Detectable Concentration
Vanadomolybdate	100	45	75.2	21.6	200 μg/l
	600	43	19.6	10.8	
	7,000	44	8.6	5.4	
Stannous chloride	100	45	25.5	28.7	3 μg/l
	600	44	14.2	8.0	
	7,000	45	7.6	4.3	
Ascorbic acid	100	3	9.1	10.0	30 μg/l
	600	3	4.0	4.4	
	7,000	3	5.2	4.9	

is mixed with a vanadate-molybdate reagent at pH 4 - 10. A yellow color develops with an intensity proportional to the PO_4-P concentration. There are a number of interferences: silica and arsenic increase the color intensity if the sample is heated; while a decrease in color intensity is caused by F^-, arsenate, Th, Bi, $S^=$ $S_2O_3^=$, SCN^-, or excess molydate. The method thus requires removal of these interferences by various means, for example, $S^=$ is eliminated by the addition of bromine water addition.

The colorimetric method is improved by mixing a molybdate reagent with PO_4-P, and then reducing the resulting molybdophosphate with stannous chloride to form an intensely blue colored complex. The molybdophosphate can be extracted into a benzene-isobutyl alcohol mxiture, thereby increasing the sensitivity and decreasing interferences.

A third method is the ascorbic acid method, also designated as the single reagent method in the EPA manual (Ref.44). It may be applied to fresh, waste, and saline waters, and is used over the range 0.01 to 0.5 mg/l phosphorus. Color development takes place in two steps: (1) solutions of ammonium molybdate and potassium antimonyl tartrate are mixed with the PO_4-P sample, and (2) this is reduced by ascorbic acid to form an intensely blue color at pH 7 ± 0.2. The minimum detectable concentration is somewhat higher than that of stannous chloride method, but solvent extraction is not required. Only arsenates, hexavalent chromium, and nitrite interfere; $S^=$ does not interfere at 1.0 mg/l, silicate does not interfere at 10.0 mg/l. The method is the only manual technique listed in the EPA manual. The ASTM book, Part 31, lists three methods, two of which are suited for fresh, saline and waste waters: ascorbic acid and amino-naphthol-sulfonic acid reduction (Ref.53).

b. Automated

The EPA methods manual lists an automated procedure using a Technicon AutoAnalyzer to measure PO_4-P. The water sample is mixed with ammonium molybdate and antimony potassium tartrate reagent to form a complex which is reduced with ascorbic acid to form a blue-colored solution. The method applies over the range 0.001 to 1.0 mg/l PO_4-P. Approximately 20-30 samples can be analyzed per hour.

The Technicon instrument system was applied by Osburn, Lemmel and Donvey to the automated analysis of PO_4-P, hydrolyzable, and total phosphate in surface and wastewater (Ref. 54). The method was developed so that it could be applied to water samples containing suspended solids (turbidity), unnatural color, and silicate. Turbidity was compensated by determining the attenuation in light intensity for samples containing all reagents; then making the same measurements for samples containing all reagents except ascorbic acid. The molybdenum blue color does not develop in the absence of ascorbic acid so that any attenuation in light intensity is related to sample turbidity. See Table D-10 for the effects of turbidity on water samples. The method was evaluated by standard addition of PO_4-P to river water samples. See Table D-11.

TABLE D-10
Effect of Turbidity on
Automated Orthophosphate Results (from Ref. 3)

Sample	Mg/l Phosphate		
	Automated		Manual
	Uncorrected	Corrected	
1	0.12	0.05	0.02
2	0.38	0.11	0.12
3	0.24	0.22	0.28
4	0.47	0.11	0.11

TABLE D-11
Ortho- and Total Phosphate in River Water
Before and After Addition of Orthophosphate (from Ref. 3)

Sample	Mg/l ortho P			Mg/l total P		
	Before	Added	After	Before	Added	After
1	0.05	0.25	0.29	0.07	0.25	0.32
2	0.05	0.25	0.25	0.06	0.25	0.28
3	0.32	0.25	0.56	0.42	0.25	0.68
4	0.15	0.20	0.32	0.20	0.20	0.40
5	0.29	0.20	0.45	0.33	0.20	0.45

Average % recovery of added orthophosphate: ortho P = 95.0, total P = 97.0.

3. Sulfur In Water

This section surveys primarily the literature on instrumental methods which are, or might be, applied to monitoring sulfate (SO_4-S), sulfite (SO_3-S), and sulfide (H_2S-S) in water. Basically, methods discussed fall into one of the following categories: (1) the standard methods currently in use; and (2) new techniques which might be more selective, more sensitive, or take less time than current standard methods. The literature covered will be selective; no attempt will be made to include all the publications on sulfur analytical methodology.

Standard Methods, 14th edition, includes gravimetric, titrimetric, turbidimetric, and colorimetric methods for determining SO_4-S, SO_3-S, and H_2S-S in water and wastewater (Ref. 11). The U. S. Geological Survey Methods, Book 5, lists titrimetric methods for SO_4-S and H_2S-S; the EPA Methods Manual lists turbidimetric, automated colorimetric and gravimetric for SO_4-S: and titrimetric for H_2S-S and SO_3-S (Ref.27); and ASTM, Part 31, Water, lists gravimetric, volumetric, turbidimetric for SO_4-S, and titrimetric for SO_3-S (Ref.36).

Sulfate

a. Gravimetric

The gravimetric method for SO_4-S is based on precipitation by Ba, as $BaSO_4$, from an acidified solution of the water sample. It is applicable to SO_4-S contents above 10 mg/l. However, the method is subject to a number of errors depending on the other constituents in the water sample. High results are caused by some constituents (e.g., silica, suspended matter, sulfite); low results by other constituents such as alkali metal sulfates. The interferences must be removed from the water sample prior to analysis (e.g., cation exchange). Standard Methods contains a detailed discussion of interfering constituents and their removal (Ref. 11).

b. Turbidimetric

In the turbidimetric method, SO_4-S is mixed with $BaCl_2$ in HCl solution to form a suspension. The resulting suspension is placed in a cell, and the scattering for light attenuation is measured using either a nephelometer or a spectrophotometer. The method is subject to interferences by dissolved color, suspended matter, > 500 mg/l silica, and organic matter. The color and suspended solids can be corrected for by measuring a water sample to which $BaCl_2$ reagent has not been added as a blank. The method has a minimum detectable limit of 1 mg/l SO_4-S.

The EPA has developed an automated colorimetric method for SO_4-S using a Technicon AutoAnalyzer (Ref. 3). The method is based on the following color-forming reaction of SO_4-S with barium chloranilate:

$$\underset{\text{(colorless)}}{\text{Ba Chloranilate}} + SO_4^{=} \rightarrow BaSO_4\downarrow + \underset{\text{(purple)}}{\text{chloranilate}}$$

The released chloranilate has a purple color for which the intensity is proportional to the concentration of SO_4-S. Interferences are removed by ion-exchange. The method may be applied for the range of 10 to 400 mg/l SO_4-S.

Some developing methods for SO_4-S analyzers are described in the review article by Fishman and Erdmann (Ref. 5). The articles reviewed show a continued interest in automated colorimetric methods. For example, a method has been developed centering around the reaction between SO_4-S and thorium-SPADNS reagent to yield a colored solution.

Sulfite

The Standard Method for SO_3-S is titrimetric, and is based on titration with an iodide-iodate solution of known concentration to a starch indicator end-point (blue color). The method can measure SO_3-S to a minimum detectable concentration of 2 mg/l.

The ASTM Book of Standards lists three titrimetric methods for SO_3-S in water. For SO_3-S over the range 0.1 to 6 mg/l, excess iodine chloride is added to oxidize SO_3-S to SO_4-S. The remaining (excess) iodine chloride is then measured by titrating with a standardized thiosulfate solution to an amperometric end-point. High results are caused by the presence of H_2S-S while NO_2-N will oxidize SO_3-S and cause low results. For SO_3-S concentrations greater than 6 mg/l, the reagent concentrations are adjusted. The end-point is detected amperometrically. The third method is similar to that in Standard Methods, 14th Edition, where the end-point is detected by starch indicator.

The EPA method for SO_3-S applies to fresh and waste waters; it is identical to the titrimetric methods given in Standard Methods and ASTM (Ref. 4).

Sulfide

The standard methods for H_2S-S are either volumetric (titration with iodine) or colorimetric using methylene blue. In the methylene blue method, paraaminodimethylaniline, ferric chloride and H_2S-S are mixed to form the methylene blue color. It is applied to concentrations covering the range 0.02 to 20 mg/l.

The titrimetric method is listed in Standard Methods, the EPA methods manual, and the USGS report. It may be applied to fresh, waste, and saline waters which have H_2S-S concentration above 1 mg/l. In this method, volatile sulfides are stripped from an acidified water sample by an inert gas (N_2, CO_2). The gas containing H_2S-S is bubbled through a solution containing dissolved Zn, to precipitate ZnS. Excess iodine and acid are added to the Zn solution to release H_2S-S, which reacts with iodine. The unreacted iodine is determined by titration with thiosulfate and is related to the quantity of H_2S-S.

Interferences include SO_3-S, thiosulfate and hydrosulfite. Care must be taken to exclude oxygen which will oxidize H_2S-S. The sample should be analyzed immediately, or it must be preserved with zinc acetate to prevent loss of H_2S-S.

Ion selective electrodes are available for sulfide monitoring.

SUMMARY AND RECOMMENDATIONS

Methods for monitoring nitrogen, phosphorus, and sulfur are given. Care must be taken in eliminating interfering substances and in the proper adjustment of parameters of the analytic procedure.

The Laboratory and field automated instruments should be investigated for use as continuous monitors and for reducing the time required for routine analyses.

E, ACKNOWLEDGMENT

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49. J. G. Holtz and H. S. Potworowki, "Brucine Analysis for High Nitrate Concentrations," Env. Sci. Tech. 6 (9), 835 (1972).

50. S. F. Bankert, S. D. Bloom, and F. S. Dietrich, "Rapid Nitrogen Tests in Water Samples in the ppb Range", UCRL-Preprint, Oct. 13, 1972, Lawrence Livermore Laboratory, Livermore, CA.

51. Nitrogen Oxide Electrode, Model 95-46, Orion Research Inc., 380 Putnam Avenue, Cambridge, MA 02139 (1973).

52. Standard Methods for the Examination of Water and Wastewater, 14th Edition, American Public Health Association, Washington, DC 20036 (1976).

53. Q. W. Osburn, D. E. Lemmel, and R. L. Downey, "Automated Method for Ortho-, Ortho-Plus Hydrolyzable, and Total Phosphate in Surface and Wastewaters," Env. Sci. Tech. 8 (4). 363 (1974).

G. NPS-in-Water Instrument Notes

TABLE OF
ULTRAVIOLET AND VISIBLE ABSORPTION INSTRUMENTATION

Instrument	Wavelength Range (nm)	Wavelength Accuracy (nm)	Wavelength Resolution (nm)	Cost	Remarks
American DW-2™	200-825	±0.2	< 0.3	$19,900.	Wavelength scanning
Baird Atomic FM-200		10		$ 845.	
FP-100	220-770	2	2	$ 4,475.	Fluorometer Automatic or manual scannning
SF-100	220-700	2	2	$ 5,975.	Spectrofluorometer 2-speed wavelength scanning
Bausch & Lomb					
Spectronic ® 20	340-950	2.5	20.0	$ 525.	Regulated model, $595.
Spectronic ® 70	325-925	1.0	8.0	$ 795.	
Spectronic ® 88	"	"	"	$ 1,195.	Concentration
Spectronic ® 100	"	"	"	$ 2,195.	Digital readout, concentration
Spectronic ® 200	190-800	±0.5	0.25	$ 4,895.	Wavelength scanning
Spectronic ® 210	190-900	"	"	$ 6,000.	Digital, wavelength scanning, concentration
Spectronic ® 700	200-950	1.0	2.0	$ 2,600.	Concentration
Spectronic ® 710	200-1000	"	"	$ 3,000.	Digital, concentration

(Continued)

TABLE OF
ULTRAVIOLET AND VISIBLE ABSORPTION INSTRUMENTATION
(continued)

Instrument	Wavelength Range (nm)	Wavelength Accuracy (nm)	Wavelength Resolution (nm)	Cost	Remarks
Beckman 24	340-700	±0.5	4.0	$ 2,730.	Wavelength scanning
25	190-700	"	0.2	$ 4,350.	Wavelength scanning
ACTA CII	190-800	±0.1	"	$ 6,680.	
ACTA CIII	"	"	"	$ 9,710.	
ACTA M-IV	190-3000	±0.5 (UV-Vis) ±2.5 (NIR)	0.02 (UV-Vis) 1.2 (NIR)	$14,445.	
ACTA M-VI	"	±0.1	< 0.05	$13,910.	
ACTA M-VII	190-800 800-3000	±0.1 ±0.5	< 0.05 < 0.30	$24,610.	
Model B	325-1000	±5.0	< 5.0	$ 2,140.	
Model DB-GT	190-700	±0.5	< 0.2	$ 3,890.	
Model DU-2	190-1000	"	< 0.3 (UV) < 0.1 (Vis)	$ 5,210.	
Brinkman 1101-M	313-772			$ 3,010.	Fluorometer
GCA/McPherson EU-701-D	185-750 185-1000 (optional)	±0.1	0.1	$ 4,255.	
EU-707	"	"	"	$ 5,800.	
EU-721-D	"	"	"	$ 5,075.	

(Continued)

TABLE OF ULTRAVIOLET AND VISIBLE ABSORPTION INSTRUMENTATION (continued)

Instrument	Wavelength Range (nm)	Wavelength Accuracy (nm)	Wavelength Resolution (nm)	Cost	Remarks
Gilford 240	185-800			$ 5,366.	
Hitachi 101	220-900	< 2.5		$ 2,030.	
102	"	"		$ 2,700.	
181-7000		< 0.5		$ 2,750.	Model 181-7100, Tungsten only $2,350.
191	195-900			$ 3,350.	
Micromedic MS 2	200-700	±1.0	0.0003A	$ 4,400.	
Perkin-Elmer Junior Series	325-825	±1.0	20	$430 to $827	
54	330-835	"	±1	$ 1,654.	
Perkin-Elmer 55	325-800 200 (optional)	±1.0	2	$ 2,811.	
124	190-800			$ 4,382	Model 124D - $ 4,272.
156	190-900				
295	400-700	±1.0 @ 610 nm		$ 381.	
323	185-2500	±0.4 (UV)	0.2 (UV)	$15,200.	
356	185-850 185-1200 (optional)	±0.5	"	$17,000.	

(Continued)

TABLE OF
ULTRAVIOLET AND VISIBLE ABSORPTION INSTRUMENTATION
(continued)

Instrument	Wavelength Range (nm)	Wavelength Accuracy (nm)	Wavelength Resolution (nm)	Cost	Remarks
402	190-850	±0.5 @ 200 nm ±1.0 @ 500 nm ±2.0 @ 750 nm	0.2 @ 210 nm 0.4 @ 390 nm 1.5 @ 600 nm	$ 8,480.	
Pye-Unicam SP 1700	190-700 850 (optional)	±0.5	0.1	$ 6,100.	Digital readout
SP 1800	"	"	"	$ 5,300.	Analog readout
Tektronix RSS	250-1100	±10 (150 1/mm) ±3 (1200 1/mm)	4 (150 1/mm) 0.4 (1200 1/mm)	$11,000.	Silicon vidicon detector
Turner 110	254-600	Blocking filters	Blocking filters	$ 1,195.	Filter photometer, manual
111	"	"	"	$ 1,735.	Filter photometer, automatic
330	335-710	±2.0	9.0	$ 595.	Spectrophotometer
350	"	"	"	$ 735.	"
430	300-700	"	15 (Excitation) 15 and 60 (Emission)	$ 3,990.	Spectrophotometer
510	Interference filters			$ 3,950.	Flame photometer
Varian Cary 17	186-2650	±0.4	0.1 (UV-Vis) 0.3 (IR)	$26,950.	Prism and grating

(Continued)

TABLE OF ULTRAVIOLET AND VISIBLE ABSORPTION INSTRUMENTATION (continued)

Instrument	Wavelength Range (nm)	Wavelength Accuracy (nm)	Wavelength Resolution (nm)	Cost	Remarks
Cary 118A	185-800		0.03 @ 200 nm 0.1 @ 350 nm	$10,900.	Manual
Cary 118B	"		"	$14,250.	Ratio recording
Cary 118C	185-800		0.02 @ 200 nm 0.1 @ 350 nm	$15,850.	Ratio recording scanning
635 M	190-900	>±0.5	0.2	$ 3,900.	
635 D	"	"	"	$ 4,950.	
Carl Zeiss PM2 D	200-1,000	1	10	$ 2,485.	
PMQ 3	185-2,500	< 0.05 @ 200 nm	0.03 (UV) 1.0 @ 600 nm	$ 6,800.70	

Biological Parameters
BIO

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FOR
DISSOLVED OXYGEN

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INTRODUCTION

"The water environment can generally be characterized as a dilute aqueous solution, containing a large variety of inorganic and organic chemical species, dissolved and in suspension, and including a variety of plant and animal life" (Ref. 1).

Although water contains a number of dissolved gases, oxygen ranks first in importance, since it is essential for the survival of fish and all aerobic organisms. It is therefore the gas most commonly measured in aquatic environments.

Most water pollutants fall into two general categories: those that are biologically degradable, thereby consuming oxygen, and those substances that persist in the aqueous environment. The best known degradable pollutant is domestic sewage which includes both inorganic and organic degradable substances; but the combined organic wastes produced by industrial sources such as the food, pulp and paper, and chemical industries comprise by far the greater source of this pollution. Organic wastes may further be subdivided into three categories:

a) those that are used as an energy source by heterotrophic bacteria* (and therefore biodegradable);

b) those inert organic substances which are neither utilizable by the resident biota, nor toxic to them, for example, many many high molecular weight synthetic organic polymers;

c) toxic organics, such as the pesticides.

Some industrial plants produce huge quantities of organic pollutants. For example, a single pulp mill discharges wastes equivalent to the sewage load of a large city (Ref. 2).

When an effluent bearing a substantial load of organic wastes is expelled into an otherwise clean stream, a process known as aerobic degradation begins immediately. Stream biota -- primarily bacteria -- utilize dissolved oxygen and feed on the wastes, decomposing them to their inorganic end products (nitrates, carbonates, phosphates, sulfates), thereby furnishing the basic plant nutrients. This process, somewhat deceptively called "stream self-purification", consumes some of the dissolved oxygen (DO) present in the water. The depletion of oxygen is, however, offset by reoxygenation both via the air-water interface (a relatively slow process in still waters), and as a consequence of photosynthetic processes occurring in the aquasystem. If the waste load is not too heavy, the concentration of DO ([DO]) will first drop, and then rise again. This process is described mathematically by a characteristically shaped function known as the *oxygen sag* (Figure 1). If the concentration of organic wastes in the stream becomes high enough, however, the supply of DO may be exhausted. Degradation will then proceed via anaerobic processes through the action of bacteria capable of utilizing organically- and inorganically-bound oxygen. The gaseous byproducts of these anaerobic processes (CH_4, NH_3, H_2S) generally result in the emission of foul odors and the production of offensively brackish waters.

Plant nutrients resulting from the bacterial degradation of organic wastes may cause algae blooms. While these are not harmful in moderate abundance, even contributing to the food supply of the resident fish, they may pose problems for the resident biota if allowed to proliferate unchecked, because of ultimate DO depletion by algae decomposition. Streams in which the DO is consistently less than four to five ppm will not support some of the higher forms of fish life, such as the cold water varieties. Reduced levels of oxygen, even when not themselves lethal, increase the sensitivity of the fish to toxins. These problems are particularly important in comparatively quiet waters, such as lakes and estuaries, where the rates of reoxygenation are likely to be low. Here eutrophication from the build-up of inorganic nutrients can be a troublesome end result.

Wastewater in which the organic wastes have not been stabilized has a higher chlorine demand†, thereby making it more costly to treat. An increase in temperature will accelerate a stream's degradation rate and reduce the DO content. A simple rule of thumb in chemical reaction kinetics is that a given rate of reaction will double for a 10°C rise in temperature. Heat therefore exacerbates the pollution problem. For this reason, the increasing number of stream electric power plants with their concomitant high heat output poses a serious problem.

---

*Bacteria may also be viewed as degradable pollutants, since the enteric infectious variety does not survive long under in vitro (stream) conditions, and chlorination of the water supply effectively destroys them. Thus the traditional scourges of polluted water -- typhoid, paratyphoid, dysentery, and gastroenteritis -- are virtually unknown in American cities. On the other hand, viruses are less amenable to treatment. It is believed that viruses in our water supplies are associated with the spread of some diseases, but at less than the epidemic levels once attributable to bacteria.

†i.e., requires more chlorine to attain the free chlorine residual necessary to kill bacteria.

1. Factors Influencing the Solubility of O_2

The solubility of oxygen in water is primarily a function of three variables: pressure (p), temperature (T), and salt content[**] or ionic strength (μ) of the solution. In natural waters the DO content is also dependent on the quantity of biodegradable organic material present, the diurnal cycle, and physical characteristics of the stream bed (e.g., gradient, rapids, pools, etc.)

1.1 Pressure Effects

Atmospheric oxygen dissolves according to Henry's Law up to four atmospheres pressure:

$$(1) \quad \frac{P_{O_2}}{P_{total}} = P = K\,[O_2], \text{ where}$$

P is the partial pressure of oxygen in the atmosphere, and K is the Henry's Law constant:

$$K = 5.98 \times 10^5 \text{ mm Hg/M/1}$$

At its partial pressure of 154 mm under STP conditions, oxygen is only sparingly soluble in pure water (2.56×10^{-4} moles/liter). However, the effect of hydrostatic pressure on the solubility of oxygen with depth has been calculated by Klotz using a thermodynamic treatment which assumes successive equilibria between the air dissolved in any given layer

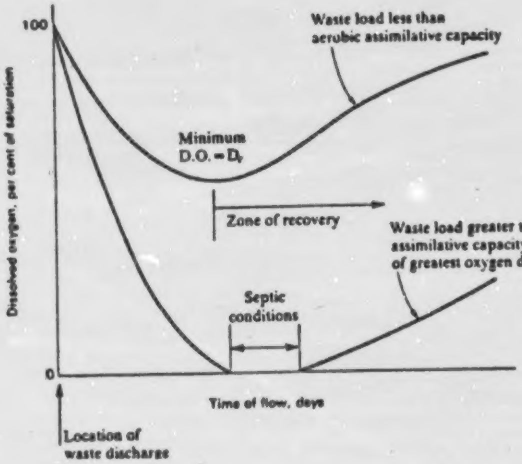


FIGURE 1[+]. Schematic primary oxygen sag curve for two different organic waste discharges, assuming waste enters a stream that is fully saturated with oxygen (from Ref. 3, p. 21).

[+] The oxygen sag equation is expressed as the difference between two kinetic processes:

$$\frac{dD}{dt} = K_1L - K_2D,$$

where L represents the oxygen demand at time t, and D the oxygen deficiency: K_1 and K_2 are proportionality constants for the deoxygenation and aeration processes, respectively (Ref. 4).

[**] The term salinity is generally employed in dealing with natural waters.

of water, dh, and that dissolved in the next adjacent layer (Ref. 5). Although the solubility of a gas may change considerably with depth, its partial molal free energy does not vary from one depth to another, being an intensive characteristic of the substance. Thus, the change in the solubility of oxygen with depth may be expressed as the following equation:

$$(2) \quad RTd\ln[O_2] = Mg(1 - \bar{v}\,\ell)dh, \text{ where}$$

h is the depth of the sample measured in a positive direction;
R is the gas constant (8.37×10^7 ergs/M/degree),
T is expressed in °K;
M is the molecular weight of the solute;
$\bar{v}$ is the partial specific volume of the solute, expressed in cc/gm;
ℓ represents the density of the solution in gm/cc, and
g is the gravitational constant ($980\ cm/sec^2$).

Integration of equation (2) over the depth h leads to the following expression:

$$(3) \quad RT\ln\frac{[O_2]_y}{[O_2]_o} = Mg(1 - \bar{v}\,\ell)h.$$

Unlike nitrogen, for which Klotz' calculation using equation (3) showed a decrease in solubility with increasing depth, the solubility of atmospheric oxygen in water appears to be relatively independent of the depth, h (Ref. 5).

1.2 Temperature Effects

As with most other gases, oxygen has a negative temperature coefficient -- e.g., decreases in solubility with increasing temperature:

$$(4) \quad [O_2] = \alpha + \beta_1 T + \beta_2 T^2 + \beta_3 T^3,$$

where T is the temperature in °C and α and β's (1, 2 and 3) are constants.† For purposes of interpolating DO saturation values at working temperatures, an approximate form of the Clausius-Clapeyron equation may be applied:

$$(5) \quad \frac{d\ln[O_2]}{d(1/T)} = \frac{\Delta H}{R}, \text{ where}$$

ΔH is the heat of solution, in calories/mole. and R the gas constant (1.99 cal/M/degree). Since the temperature dependence of ΔH is slight, the application of this relationship over a limited temperature range is approximately linear. Integration of (5) yields:

$$(6) \quad \frac{[O_2]_2}{[O_2]_1} = \frac{\Delta H}{2.3R}\ \frac{1}{T_1} - \frac{1}{T_2}$$

1.3 Electrolyte Effects

The addition of electrolytes to water generally decreases oxygen solubility, the amount of this decrease depending on the ionic strength of the solution. This phenomenon is known as the 'salting out effect' (Figure 2). The phenomenon of salting out is best understood in terms of activity coefficients*, and the effective concentration of the dissolved gas. The activity of oxygen in solution may be defined as follows:

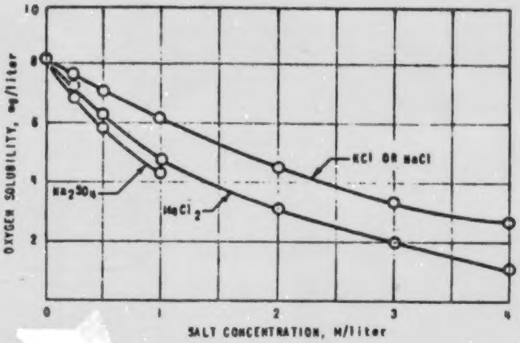


FIGURE 2. Oxygen solubility at various salt concentrations (from Reference 6, p. 6).

$$(7) \quad a = \gamma C, \text{ where}$$

a = activity in moles/liter;
γ is the activity coefficient, and
C is the concentration in moles/liter.

The activity coefficient γ depends on the ionic strength of the solution:

$$(8) \quad \ln\gamma = K_S I, \text{ where}$$

$K_S I$ is the 'salting out' coefficient, and
I the ionic strength of the solution.

---

†$\alpha = 14.161$; $\beta_1 = -0.3943$; $\beta_2 = 0.007714$; $\beta_3 = 0.0000646$

*For a discussion of the thermodynamic significance of activity coefficients, see appendix E, Reference 6.

Also,

(9) $I = \Sigma C_i Z_i^2$, where

C_i is the concentration of the ith salt component, and
Z_i is the ionic charge of the ith component.

For distilled water, $I = 0$ and $\ln \gamma$ is consequently 0 and $\gamma = 1$ (e.g., the activity is equal to the concentration).

A convenient equation for expressing the solubility of oxygen as a function of the concentration of a single salt is given:

(10) $\ln S = \ln S_o - K_s C_s$, where

S is the solubility of oxygen in the saline solution,
S_o its solubility in distilled water,
C_s is the concentration of the salt, and
K_s is a solubility constant.

A semilog plot of equation (10) is linear with a negative slope, $-K_s$. For solutions containing more than one salt, equation (8) must be used.

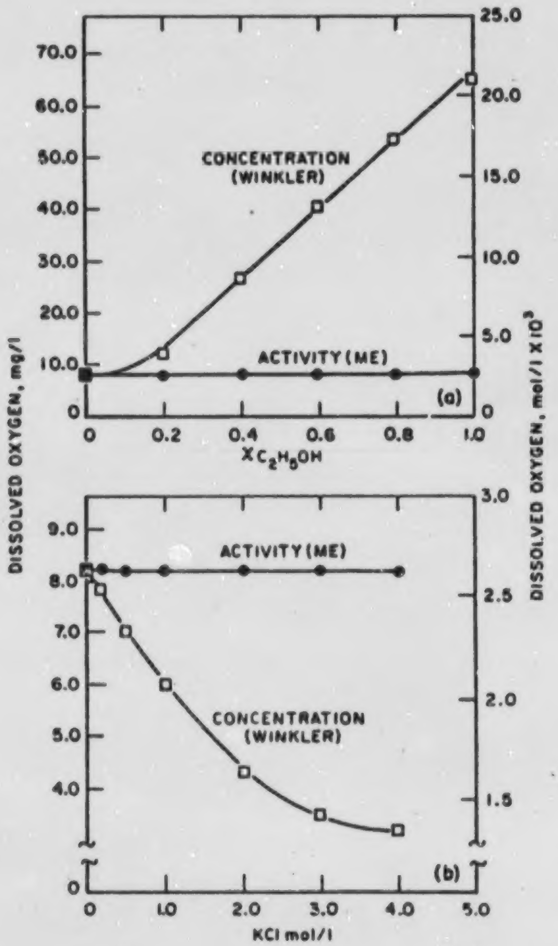


FIGURE 3. Effects of (a) salting-in and (b) salting-out. P^0_2 = 0.21 atmosphere, temperature = 25 ±0.5°C (from Reference 11, p. 314).

1.4 Effects of BOD[*] and Diurnal Variation

During daylight hours, photosynthesis produces O_2, and if its production exceeds the respiration rate, the concentration of DO [DO] will increase during the day. The entire biotic community requires O_2 at night, so that the minimum [DO] is reached just before dawn. The amount of diurnal variation is greater in organically enriched or polluted waters, where daytime supersaturation may be offset by oxygen concentrations approaching zero in the hours just before sunrise.

1.5 Other Effects

Water movement can have a significant effect on [DO] by accelerating the rate of loss at supersaturation and the rate of reaeration at low oxygen tension. Diurnal variation of DO is usually greatest in quiescent lakes and ponds, and least noticeable in rapidly flowing streams.

2. Analysis of Water for DO

Because of the constant demand for O_2 by the biotic community, the minimum $[O_2]$ and its duration are more important than measures of the average or maximum $[O_2]$. Measurements of the diurnal change of DO are useful in evaluating the overall metabolism within a body of water, encompassing both photosynthesis and respiration. Periodic measurement of this parameter often yields more information as to the condition of the body of water in question than the measurement of a large number of other environmental variables (Ref. 7).

The selection of an analytical procedure will largely depend on the objectives of the DO analysis. These may range all the way from (1) investigation of compliance with official standards, (2) evaluation of the environmental impact of a proposed water resource project, (3) assessment of the water treatment required in order to maintain a water quality level consistent with ongoing and/or proposed uses, to (4) simply providing some water quality control.

Differing objectives lead to the requirement of methods and instrumentation at varying levels of sophistication. Each analysis presents unique problems, not only in terms of the objectives of the analysis, but because water sample characteristics can vary widely, even within a given category of application. Thus, in addition to considering the needs for such characteristics as speed, accuracy, and continuity or frequency, the analyst must consider the unique character and limitations imposed by the specific water sample.

Methods used in the analysis of water samples for DO may be divided roughly into two categories:

a) Those traditional wet-chemical methods based on the Winkler test and more recent instrumental modifications of these (sections 2.2 - 2.4, inclusive);

b) Other methods based on the chemical and physical properties of oxygen and employing a wide variety of often quite sophisticated techniques and instrumentation (sections 2.5 ff.)

It is from category b) above that DO monitoring systems derive. These systems may be characterized as:

1) *in situ*[†] sensors or electrochemical transducers which perform measurements without altering the test solution, and

2) systems such as the Technicon Autoanalyzer which perform automated wet-chemical analysis.

Since *in situ* DO determination is so significant for ascertaining water quality, it is clear that emphasis should be placed on those methods which lend themselves to this kind of measurement. Such methods are invariably based on electrochemical reactions, with membrane electrode (ME) systems emerging as the most suitable vehicles for *in situ* DO analysis of natural and waste waters.

2.1 Sampling Methods for DO Analysis

Because of the diurnal variation in DO in natural systems, continuous monitoring of this parameter is desirable. If, however, continuous monitoring is not feasible, it is recommended that the [DO] should at the very least be measured twice daily -- at mid-afternoon and just before dawn.

---

[*] BOD = Biochemical Oxygen Demand

[†] in position -- generally (though not necessarily) in stream.

Samples for DO determination are generally collected in narrow-necked glass-stoppered (G.S.) flasks of 200 to 300 ml capacity, with flared rims, called BOD bottles. Great care must be exercised in the collection of samples for DO analysis to avoid agitation or post-sampling contact with air, in order to minimize the risk of oxygen exchange. The method of sampling is influenced by the source of the sample, the depth from which it is to be taken, and even the method of analysis to be used. King (Ref. 7) suggests the use of special samplers such as the Kemmerer water sampler or the Nansen water bottle for the collection of all water samples to be used in the determination of DO, in order to avoid oxygen exchange between the sample and the atmosphere. "Standard Methods" (Ref. 8) recommends the Kemmerer-type (Figure 4) sampler for all samples collected from depths of more than five feet. In the latter instance the sample is bled from the bottom of the sampler through a tube reaching to the bottom of a 250-300 ml BOD bottle. The bottle is filled to overflowing, then allowed to overflow for about 10 seconds, great care being exercised to avoid turbulence and bubble formation during the bottle-filling operation. Water temperature is recorded with the desired precision.

Depth sampling requires special precautions to eliminate effects of pressure and temperature changes. Techniques of sampling waters under pressure, as well as surface waters, are described in detail in references 9 and 10.

Selection of a sampling site is determined primarily by two factors: (a) the type of investigation, and (b) the degree of mixing in the body of water to be analyzed. Rainwater and Thatcher (Ref. 10) recommend the use of a 3-dimensional grid intersection method of sampling, with samples taken at various depths to provide a representative sampling. If only a single sample is to be taken, it should come from the center of the water mass.

Sampling frequency is determined by the variability of the source sampled. No important change in quality of the water should go unnoticed in an adequately planned sampling procedure. The U.S. Geological Survey follows the arbitrary rule for sampling once per day.

Sampling equipment is made from a variety of materials. Containers of hard rubber, polyethylene, and a few other plastics have been found satisfactory. No appreciable difference in the following characteristics was detected for pyrex vs polyethylene containers: silica content, Na^+, alkalinity, Cl^-, boron, specific conductance or pH, when water samples were stored for about five months.

Soda lime glass sampling bottles are, of course, not recommended when the samples are to be stored, because of the risk of sample contamination through leaching of ions from the glass and/or ion exchange between the glass and the water sample.

2.11 Post Sampling Preservation

The determination of DO in samples with an appreciable oxygen demand (OD) or iodine demand (ID) should be immediate -- preferably, on site. Samples which have no ID may be stored safely for several hours, provided that they are pretreated with the reagents used in the Winkler method of DO analysis, namely $MnSO_4$ solution followed by alkali-iodide solution and sulfuric acid. The pre-treated sample may then be safely stored in the dark before titration. For those samples which do have an ID and cannot be analyzed immediately, the addition of concentrated H_2SO_4 (0.7 ml) and 1.0 ml of a solution containing two grams of sodium azide (NaN_3) per 100 ml of distilled water will preserve them for four to eight hours. This treatment arrests the biological activity, thereby stabilizing the DO content, if the bottle is stored at its collection temperature, or, alternately, if it is water-sealed and stored at 10°-20°C (Ref. 8).

2.12 Post-Sampling Separation and Concentration

As with other dissolved gases, the DO in natural and waste water samples may be separated by vacuum degasification or by one of several stripping techniques. Stripping entails gas-liquid extraction by means of an inert carrier gas which is bubbled through the solution, entraining the dissolved gas from the solution into the vapor phase. The efficiency of the transfer process depends on such factors as the degree of mixing of the solution and carrier gas, and the area of the gas liquid interface.

Gaseous exchange separation of O_2 may by carried out continuously or in a batch process. In one design, a continuous mixed stream of the sample and carrier gas (N_2 or H_2) is forced through a nozzle under 50 pounds pressure. In another, the gas is stripped from the solution by means of multiple spinning discs rotating at high speed. The stripped O_2 may then be examined by gas-chromatography. By the choice of appropriate detectors, it is usually possible to analyze for a mixture of gases, including oxygen, in an aqueous sample (Ref. 11).

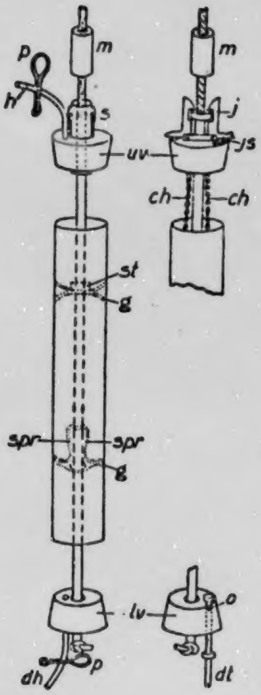


FIGURE 4. Modified Kemmerer sampler (from Ref. 8, p. 728).
Left: View of complete sampler with valves open.
Top right: another type of construction of upper valve and tripping device.
Bottom right: another type of construction of lower valve and drain tube.

Key:
ch -- chain which anchors upper valve to upper interior guide;
dh -- rubber drain tube;
dt -- brass drain tube;
g -- interior guide fastened to inner surface of body of sampler;
h -- rubber tube;
j -- jaw of release;
js -- jaw spring;
lv -- lower valve;
m -- messenger;
o--- opening into interior of drain tube;
p -- pinchcock;
s -- upper release spring operating on horizontal pin, one end of which fits into groove on central rod;
spr -- spring fastened to lower internal guide and operating in groove on central rod to provide lower release;
st -- stop on central rod;
uv -- upper valve

2.2 Chemical Methods of DO Analysis

The most widely used analytical method for DO determination is that described by L.W. Winkler over 80 years ago (Ref. 12). It is based on the quantitative oxidation of manganous ion (MnII) by DO to the manganic state (MnIV) in alkaline solution. The Mn(IV) formed liberates iodine (I_2) quantitatively from potassium iodide under acid conditions. Titration of the liberated I_2 with a standardized thiosulfate solution in the presence of a starch indicator gives a measure of the DO present in the original sample. The following is a schematic representation of the reaction sequence of the Winkler test:

$$\text{(11)}\quad Mn(II) \overset{2OH^-}{\rightarrow} \underset{\text{(white ppt)}}{Mn(OH)_2} \rightarrow \underset{\text{(colloidal suspension)}}{MnO\cdot H_2O}$$

$$\text{(11a)}\quad MnO\cdot H_2O \xrightarrow[2H_2O]{O_2} \underset{\text{brown}}{Mn(OH)_4} + 2OH^-$$

$$\downarrow$$

$$Mn(IV)O_2\downarrow + 2H_2O$$

$$\text{(11b)}\quad Mn(IV) + 2I^- \overset{H_3O^+}{\rightarrow} Mn(II) + I_2$$

$$\text{(11c)}\quad 2S_2O_3^{=} + I_2 \xrightarrow[\text{indicator}]{\text{starch}} 2I^- + S_4O_6^{=}$$

Because of its reliability and sensitivity (±0.1 mg/l of DO) (Ref. 8), the Winkler test remains the basis for most of the current titrimetric methods.

2.21 Interferences in the Winkler Method

In applying the iodometric method to natural or waste waters, the analyst must be wary of other oxidants or reductants in the sample. The presence of some oxidizing agents other than O_2 will also liberate iodine from KI, resulting in positive interference. Reductants capable of reducing I_2 to I^- will lead to low DO values (negative interference). Surface active substances present in the water sample, such as detergents, may also interfere in the analysis by keeping the hydrated MnO_2 in suspension, hampering observation of the endpoint when a starch indicator is used. A number of modifications of the Winkler DO analysis have been developed to overcome these difficulties. The most commonly used of these are described briefly in Sections 2.22 to 2.25.

2.22 Azide Modification of the Winkler Method

This procedure was recommended by Alsterberg (Ref. 13) to eliminate interference from nitrites, commonly present in waste water samples. Nitrites are reduced by sodium azide in acid solution as shown:

$$\text{(12)}\quad N_3^- \xrightarrow{H^+} HN_3 \xrightarrow{NO_2^-,H^+} N_2 + N_2O + H_2O$$

2.23 Rideal and Stewart Modification of the Winkler Method (Ref. 14).

When both nitrates and organic matter are present in the DO sample, it is pretreated with an acid $KMNO_4$ solution which removes the following reductants:

$$\text{(13)}\quad 5NO_2^- + 2MNO_4^- + 6H^+ \rightarrow 5NO_3^- + 2Mn(II) + 3H_2O$$

$$\text{(13a)}\quad 5RCHO + MnO_4^- + H_3O^+ \rightarrow 5RCOOH + Mn(II) + 3H^+$$

$$\text{(13b)}\quad 5Fe(II) + MnO_4^- + 8H^+ \rightarrow 5Fe(III) + Mn(II) + 4H_2O$$

If more than 5 mg/1 of ferric salts result after the permanganate treatment, ferric ion is removed as FeF_3. Excess permanganate is destroyed by potassium oxalate in acid solution. The Rideal-Stewart modification generally results in low accuracy and precision because of the manipulative complexity of the method.

2.24 Flocculation Modifications

Since suspended solids may result in positive interference in the Winkler test by the consumption of additional iodine, the solids are usually settled out first by means of flocculating agents. One method entails precipitation by the addition of alum and ammonium hydroxide (the Alum Flocculation Modification). Another is recommended for samples from biological treatment units, such as activated sludges. This precipitates the floc with a copper sulfate solution to which sulfamic acid, NH_2SO_2OH, is added to inhibit biological activity. The accuracy of this method is reportedly low (Ref. 6).

2.25 Other Modifications

The reader is referred to Chapter 3 of Reference 6, which lists approximately a dozen additional modifications of the basic Winkler approach, covering such exigencies as:

1. The hydrolysis of organic matter at high pH to create a false oxygen demand.
2. Analysis of "supersaturated" water samples.

3. A reversed reagent addition method.

4. A number of colorimetric variants.

2.26 Errors in the Winkler DO Method

The crucial step in analysis for DO by this method is determination of the quantitatively released free I_2 which may be carried out titrimetrically or colorimetrically. For the procedure recommended in the Standard Methods (Ref. 8), the reaction is represented by the oxidation of thiosulfate ion to tetrathionate ion and reduction of molecular I_2 to I^-:

$$(14) \quad I_2 + 2S_2O_3^= \rightarrow 2I^- + S_4O_6^=$$

When the endpoint is determined visually by the blue color formed by starch and iodine, as little as 10^{-5}M molecular I_2 may be determined. However, there are two main sources of error in the direct titration of iodine: the first is due to (a) the low solubility of I_2 in aqueous solutions (1.33×10^{-3}M/1 @ 20°C), and (b) its high volatility. The second error is the susceptibility of iodide ion (I^-) to air oxidation. This latter reaction is strongly pH dependent, catalyzed by a number of ions (including Cu(II)) and may be photochemically induced as well.

The use of alternative instrumental methods of titration reduces the likelihood that these errors will occur.

2.3 Instrumental Variants of the Winkler Procedure.

Electrochemical endpoint detection in the Winkler titration procedure not only reduces the likelihood of the errors mentioned under section 2.26, but increases the precision, accuracy and sensitivity of the method.

2.31 Potentiometric Endpoint Detection

The endpoint of the iodometric titration in the Winkler DO procedure may be determined by means of a Pt wire electrode and a saturated calomel reference electrode. At the stoichiometric endpoint, the titration curve shows an inflection point (Figure 5).

2.32 "Dead Stop" Endpoint Detection

The "dead stop" endpoint is characterized by the cessation of current flow in the cell (see diagram, Figure 6a). The method utilizes a small potential difference between two identical smooth platinum electrodes (15 to 400 mV) placed in the solution (Figure 6b). In the course of the titration, faradaic current is measured at a fixed potential difference. While I_2 remains in solution as I_3^-, the chief

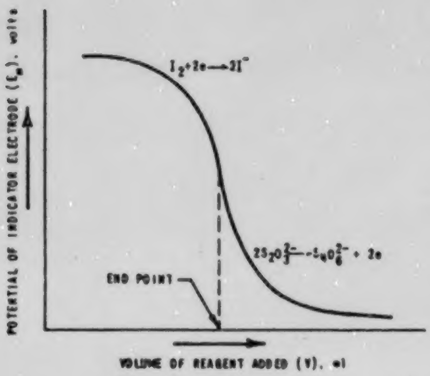


FIGURE 5. *Potentiometric titration of iodine (from Ref. 6, p. 15).*

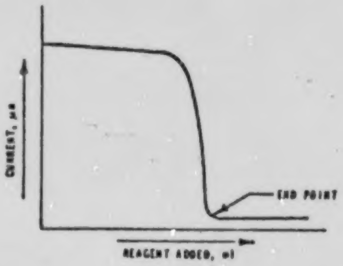


FIGURE 6a. *Dead stop end point titration curve (from Ref.* 21 *, p. 265).*

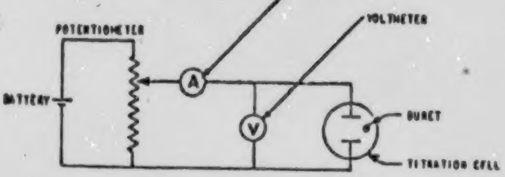


FIGURE 6b. *Dead-stop end point circuit (from Ref. 21, p. 264).*

electrode reactions are:

1) reduction of I_2 to I^- at the cathode, and

2) the oxidation of I^- at the anode.

At the endpoint, I_2 has been removed, precluding the I_2 to I^- reaction; therefore no current can flow. With the use of sensitive current detectors, the method is good to 1 part/10 billion (±0.01 ugm/100 ml).

2.33 Coulometric Titration

In a coulometric titration the reagent is electrolytically generated at the surface of the working electrode (anode) immersed in the solution (Figure 7). The amount of iodine generated may be calculated from Faraday's Law which states that, for the passage of one Faraday (96,500 coulombs) of current through the solution, one gram equivalent of I_2 will be produced:

(15) $W = \frac{qM}{nF}$, where

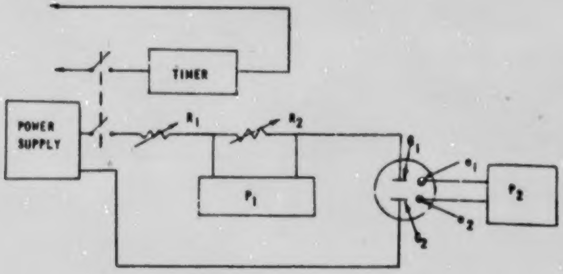
W is the weight of Iodine in grams,
M is the molecular weight of I_2 (253.8 g/mole)
q is the amount of current passed through the solution in coulombs
n is the number of equivalents per mole (or the number of electrons involved in the half-cell reaction).

In order to simplify the instrumentation and produce values directly proportional to time, most coulometric titrations are carried out at constant current. Under these conditions,

(16) $q = \int_0^t i\,dt = it$, where

t is expressed in seconds, and i is the constant current in amperes x 10^{-6}. Figure 7 illustrates a typical constant current coulometer. The procedure for the coulometric determination of DO in a water sample involves the stepwise addition of $MnSO_4$, KOH + KI, and H_2SO_4, and, finally, an excess of $Na_2S_2O_3$. The iodine formed in the electrolytic reaction reacts with the excess thiosulfate present. Current is held constant by applying a high voltage through a large dropping resistor. The equivalence point may be conveniently detected by means of the dead-stop endpoint mentioned previously (section 2.32). The concentration of DO is then calculated from equations (15) and (16) above. Since i is kept constant, q may be determined by a substitution of the time t in the equation.

Coulometric measurement in the Winkler procedure has the advantage of great accuracy, and determinations may be made to within 0.02 μgm/l. Since the titrant is generated in situ, error due to contact with air is eliminated.



R_1, R_2 = Resistors

P_1 = Potentiometer for current measurement

P_2 = Potentiometer for end point detection

e_1, e_2 = Monitoring electrodes

G_1 = Generating electrode

G_2 = Auxiliary electrode

FIGURE 7. Constant-current coulometric circuit (from Ref. 21, p. 266).

2.34 Analysis for DO Using a Micro Winkler Adaptation

The Macro Winkler method described in in Standard Methods has been adapted to small volume samples, and for use in biological systems, where repeated DO measurements, each involving the removal of a small volume of sample are required. This modified micro method uses one to two ml of water and has an accuracy of 1 to 2%. The apparatus consists of a syringe type pipet (Figure 8), in which the sample and reagents are mixed. The liberated I_2 is then expelled for titration. For details of this procedure, see Appendix B, Reference 6.

2.4 Colorimetric Methods of DO Determination

The iodine liberated in the Winkler analysis may be estimated colorimetrically in a variety of ways: (a) The blue color of the starch-iodine complex can be measured photometrically (Ref. 15); (b) the liberated iodine may be estimated spectrophotometrically at 450 mμ (Ref. 16); (c) alternately, the free iodine may be extracted from the aqueous solution into CCl_4 and determined photometrically using disc comparators (Ref. 16).

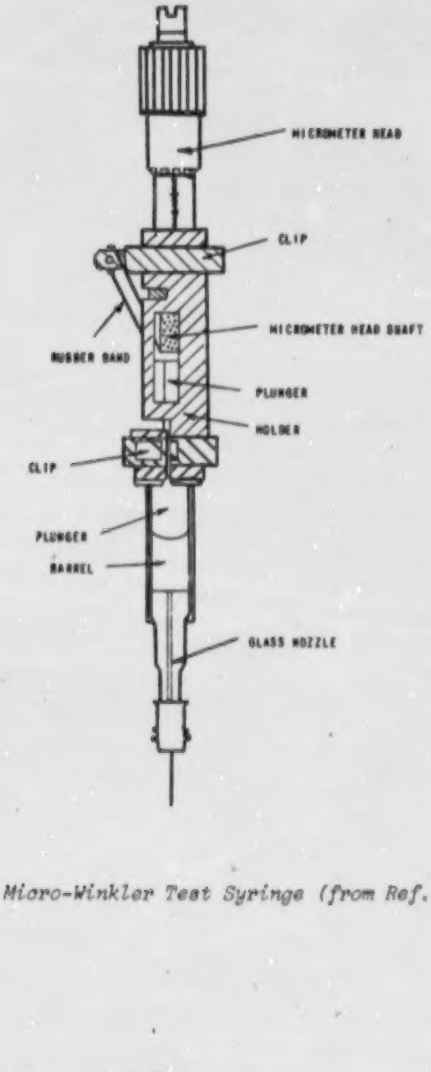


FIGURE 8. Micro-Winkler Test Syringe (from Ref. 6, p. 21).

2.41 Direct Colorimetric Methods of DO Determination

These methods generally depend on the the reaction of DO with a chromogen to give a color change. Oxidation-reduction indicators such as methylene blue, safranin T, and indigo carmine are employed (Ref. 6). The latter is the basis of an accurate method for DO analysis in boiler waters (Ref. 17).

2.42 Interferences with Colorimetric Methods of DO Analysis

Reportedly, nickel, copper (Cu(II)), and zinc do not interfere when present up to 1000 ppb, ferric ion up to 3000 ppb, and sulfite, 12 ppb. Ferrous ions do interfere, but may be removed on an ion exchange column (Ref. 18), although the oxidizing and/or reducing agents present in waste water precludes the use of a direct colorimetric aprroach. However, in comparatively clean surface waters, direct colorimetric methods can be useful.

2.43 Disadvantages of DO Direct Colorimetry

(1) When reduced indigo carmine is the indicator, 'anaerobic' sampling methods must be used to avoid exposing the sample to atmospheric oxygen. This poses difficulties in the field.

(2) There are no methods extant for *in situ* DO determination using direct colorimetry.

(3) Direct DO colorimetry does not lend itself to a continuous monitoring approach, and finally,

(4) Colorimetric methods are destructive.

2.5 Ion-Exchange Titrimetric DO Analysis

Inczedy (Ref. 19) describes an ingenious cation exchange resin method applicable to pure water only. The resin is first converted to the ferrous form with 0.1 N ferrous ammonium sulfate. The sample is then put through the column where it oxidizes an equivalent amount of Fe(II) to Fe(III). The column is treated with 6N H_2SO_4 eluting both ions. Titration of the remaining unoxidized Fe(II) with permanganate yields the value for DO by difference, since DO is equal to the equivalents of Fe(III) formed in the column by oxidation.

The following substances interfere with the test: (1) oxidants, (2) complexing agents, and (3) solids. The method is therefore only applicable in the analysis of water of high purity.

2.6 DO Analysis by the Gas Exchange (GE) Method

The determination of DO in the gas phase has the advantage of circumventing interferences often encountered in the original solution. A typical oxygen analyzer consists of (a) a gas exchange unit, and (b) an oxygen detector (Figure 9).

2.61 The Gas Exchanger

The gas-exchange unit usually consists of an aspirator followed by a separator. The water sample, along with a carrier gas inert to oxggen under conditions of the analysis (N_2 or H_2) is forced through a nozzle at about 50 lbs. pressure. Under these conditions intimate mixing of the gas and water droplets occurs and the DO is transferred to the gas phase. The efficiency of gas exchange will depend on the efficiency of the GE unit itself. Since equilibrium in the gas partition may not be obtained, the flow rates of the components must be constant in order to stabilize the rate of gas exchange. On leaving the GE unit, the carrier gas is passed through the detector and is either vented to the atmosphere or recirculated (Ref. 20). If the carrier gas is recirculated, equilibrium is eventually attained between the gaseous and aqueous phases, at which time the oxygen in the solution may be assumed to have been completely replaced by the carrier gas. (Ref. 22, 23).

2.62 The Oxygen Detector

The entrained oxygen may be detected by one of three methods: (a) by means of an oxygen-sensitive galvanic cell; (b) by a paramagnetic oxygen detector, or (c) by virtue of its thermal conductivity characteristics.

Method (a): Oxygen-sensitive galvanic cells consist of a base metal anode such as Zn, Pb, or Cd; the cathode may be a noble metal such as Au, Ag, or Ni; alternatively, a carbon cathode may be used. A highly conducting electrolyte in solution such as KOH is used. The carrier gas with entrained oxygen is bubbled through the solution by means of diffusers. The oxygen goes into solution and is depolarized at the cathode, generating an equivalent amount of current (Ref. 25). Measurement is generally with a micro-ammeter previously calibrated in terms of oxygen.

For an O_2-sensitive galvanic cell consisting of a Zn-C couple and KOH solution (1 M), the following half-cell reactions may be written:

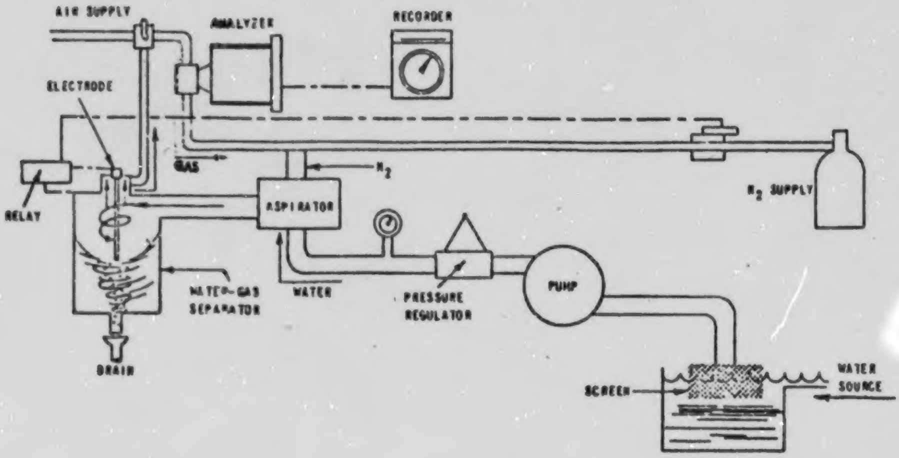

AIR SUPPLY
ANALYZER
RECORDER
ELECTRODE
GAS
N_2
RELAY
ASPIRATOR
N_2 SUPPLY
WATER-GAS SEPARATOR
WATER
PRESSURE REGULATOR
PUMP
DRAIN
SCREEN
WATER SOURCE

FIGURE 9. Gas-exchange analyzer (from Ref. 6, p. 25)

Anode: (17) $Zn \rightarrow Zn(II) + 2e$

(18) $Zn(II) + 4OH^- \rightarrow ZnO_2^{2-} + 2H_2O$

Cathode: (19) $1/2\ O_2 + H_2O + 2e \rightarrow 2OH^-$

Overall Cell Reaction:

(20) $Zn + 2OH^- + 1/2\ O_2 \rightarrow ZnO_2^{2-} + H_2O$

Method (b): Magnetic Oxygen Detector. Unlike most gases oxygen is strongly paramagnetic, making possible a detector based on the measurement of the magnetic susceptibility of the entrained gas mixture. In practice, the carrier gas leaves the exchange unit, passes through the oxygen detector consisting of a cell fitted with a permanent magnet and a spiral wire which is heated during operation (Figure 10). The heated oxygen gas loses its magnetic properties and is replaced inthe field by the cooler paramagnetic oxygen, thereby setting up a circulation of the O_2 gas in the vicinity of the heated wire. The change in resistance brought about by the flow of the cooler O_2 is proportional to the total amount of O_2 present in the carrier gas stream. This in turn depends on the DO present in the original test solution.

A second method for the magnetic determination of O_2 utilizes a small glass dumbbell suspended from a taut quartz fiber in a non-uniform magnetic field (Figure 11). In the absence of O_2, the force of the magnetic field and the torque exerted by the dumbbell

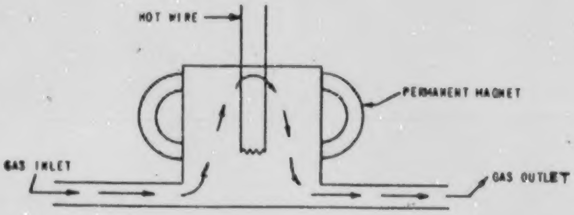

HOT WIRE
PERMANENT MAGNET
GAS INLET
GAS OUTLET

FIGURE 10. Paramagnetic analyzer cell (from Ref. 21, p. 270).

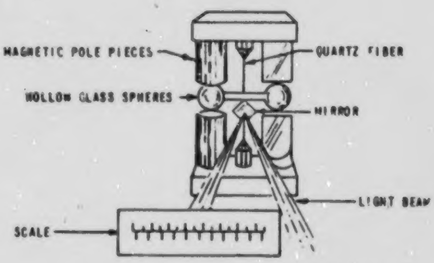

MAGNETIC POLE PIECES
QUARTZ FIBER
HOLLOW GLASS SPHERES
MIRROR
LIGHT BEAM
SCALE

FIGURE 11. Oxygen-sensitive paramagnetic detector (from Ref. 21, p. 271).

remains stationary. On introduction of a carrier gas containing oxygen, the change in the magnetic field results in an imbalance of forces and the dumbbell rotates. The magnitude of the rotation is proportional to the change occurring in the magnetic field, the latter depending on the [O_2]. Thus the amount of O_2 in the carrier gas, and consequently the DO present in the original sample is determined.

Method (c): Thermal Conductivity Detector. A thermal conductivity type O_2 detector utilizes a wire which has a high temperature coefficient of resistance. The wire is stretched along the axis of a cylinder made of glass or metal, after which it is connected to a wheatstone bridge type circuit (Figure 12). Current passing across the bridge heats the wire, the equilibrium temperature of which depends on the thermal conductivity of the surrounding gas. Any change in thermal conductivity of the carrier gas produced by exchanged oxygen present will unbalance the bridge. This imbalance may then be measured either by a galvanometer or a potentiometer calibrated against standard DO solutions.

2.63 Merits and Disadvantages of GE Analyzers

Merits:

(1) Interferences are eliminated - in particular, those of salts and organics commonly present in waste waters.

(2) GE analyzers may be adapted for continuous monitoring of DO.

(3) The units described may be used in the field, whether on the bank of a stream or alongside an activated sludge unit.

Disadvantages:

(1) GE analyzers cannot be used for in stream determination of DO.

(2) They lack portability and are not sufficiently rugged to permit mounting the units in a boat. This precludes their use for river surveys.

(3) GE oxygen analyzers are not suited for discrete laboratory sample analysis.

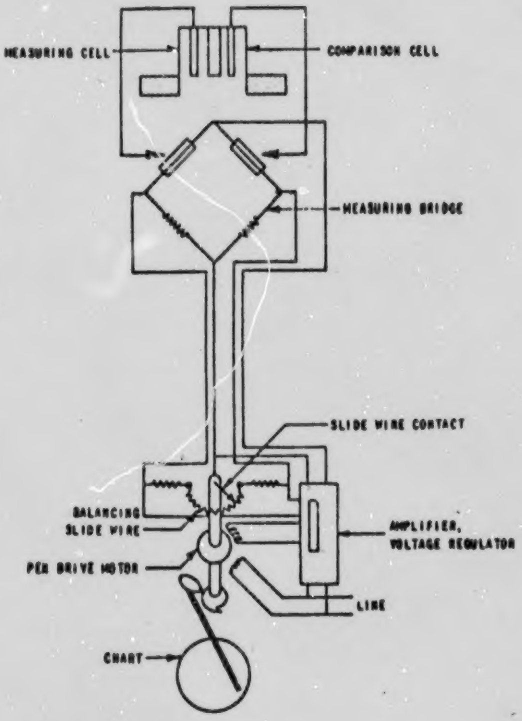


FIGURE 12. Schematic diagram of thermal conductivity oxygen analyzer (from Ref. 6, p. 28).

2.64 Performance of GE Analyzers

Oxygen analyzers of this type have accuracies of ±2 to ±5% of their full-scale readings. For DO values in the range of 0 to 5 mg/l, the expected accuracy for full-scale deflection is thus between 0.1 and 0.25 mg/l. Precision is of the order of ±1% of full-scale deflection.

2.7 Gas Chromatographic (GC) Methods of DO Analysis

In the GC determination of DO, the gas must first be stripped from aqueous solution by means of an inert gas. This is accomplished in a GE unit which is composed of a number of spinning discs capable of rotating at high speed while partially immersed in water. Such a unit has the capability of purging water of dissolved gases in a single pass over a wide range of inert gas-to-water flow ratios (See Figure 13).

From the GE unit, the gaseous stream passes through two GC columns arranged in series. The diagram in Figure 14 represents the Fisher gas partitioner (model 25). Chromatographic separation into the component gases is followed by passage of the gas through the detectors which are thermal conductivity cells. Elution curves are recorded by means of a 10 mV full-scale recorder.

The Fisher analyzer is calibrated as peak height (mm) vs gas volume ml/l. Using helium (He) as the carrier gas, good partitioning was achieved; however, the partitioner was unable to separate argon (Ar) from O_2. Another procedure entails the analysis of duplicate samples, in one of which O_2 is removed by catalytic combusion or absorption before column chromatography is used (Ref. 26). The difference between the samples is a measure of the oxygen present.

2.71 Evaluation of the GC Method for DO Analysis

GC has the following advantages for DO analysis:

(1) In common with other GE methods, it eliminates those interferences which cause analytical difficulties in aqueous DO analysis.

(2) The GC method is an on-stream one, and can be adapted for continuous monitoring.

(3) The method has multiparameter capability, enabling the analyst to determine other gases present in the original solution as well as O_2 (e.g., CO, CO_2, H_2, CH_4).

GC has these disadvantages for DO analysis:

(1) The instrumentation is delicate and complicated, requiring the attention of a specialist.

(2) In stream analysis for DO is not feasible.

(3) The GC Analyzer does not have the ruggedness or portability desirable in field use equipment.

2.8 Other Gasometric Methods of DO Analysis

Theriault and McNamee (Ref. 27) describe a modified gasometric method based on the Van Slyke* procedure which has since undergone some further modification (Ref. 28).

Prior to gasometry, gases are vacuum stripped from the solution to be analyzed, and transferred to a reaction vessel containing the Winkler DO test reagents. The mixture is then shaken for 15 minutes or more to complete the reaction, after which it is titrated with thiosulfate solution as usual. Details of this method are given in the Appendix C of Reference 6. McKeown and co-workers have made a study of the effects of a number of variables such as sample volume, stripping time and reaction time. There appears to be a good correlation between the Standard Winkler Test and the gasometric variant of it in distilled water samples with levels above 1.0 mg/l. Below the 1.0 mg/l level considerable error may result from turbulence developed during sample transfer to the gasometer. The method has an accuracy of ±0.2 mg/l.

2.81 Advantages and Disadvantages of Gasometric DO Analysis

Gasometry is essentially a GE method, since the oxygen determination is carried out on the gas phase. As with other GE methods, it, too, avoids the pitfalls of interference by ionic species as well as non-volatile organics. However, volatile species such as H_2S, which interfere with the Winkler analysis are not excluded.

Chief disadvantages of the gasometric approach are:

(1) Gasometric equipment is not readily adaptable to a continuous monitoring process for DO, and

(2) The method is a laboratory analysis, not applicable in the field.

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*A manometric procedure for the measurement of gases dissolved in blood. See Reference 29.

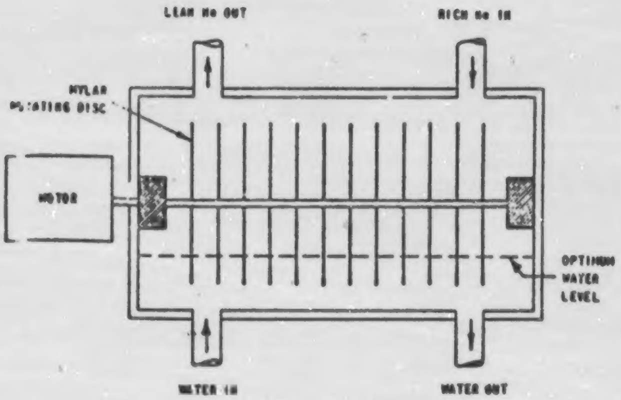
LEAN He OUT
RICH He IN
MYLAR
ROTATING DISC
MOTOR
OPTIMUM
WATER
LEVEL
WATER IN
WATER OUT

FIGURE 13. Gas exchange unit (from Ref. 6, p. 30).

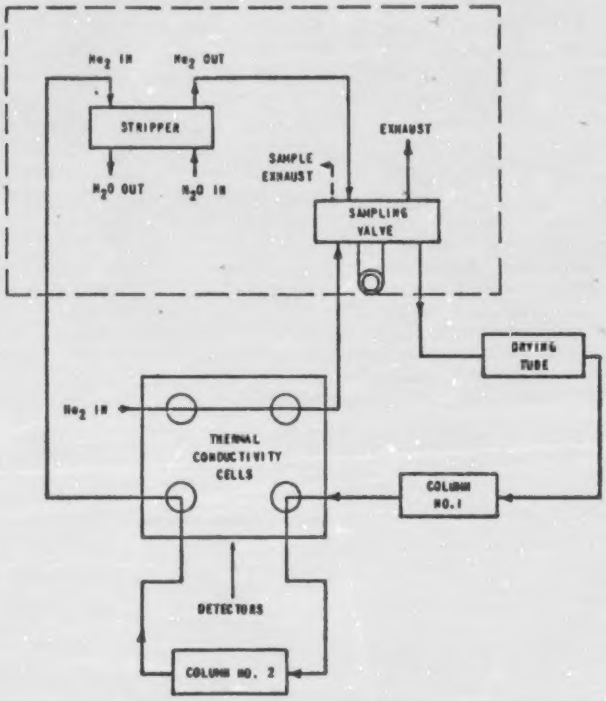
He_2 IN
He_2 OUT
STRIPPER
H_2O OUT
H_2O IN
EXHAUST
SAMPLE
EXHAUST
SAMPLING
VALVE
DRYING
TUBE
He_2 IN
THERMAL
CONDUCTIVITY
CELLS
COLUMN
NO. 1
DETECTORS
COLUMN NO. 2

FIGURE 14. Gas chromatographic analyzer (from Ref. 21, p. 274).

2.82 Micro-Adaptation of the Gasometric Method

This adaptation permits the analysis of as little as 1 ml of a water sample. The method involves stripping of the dissolved gases in a specially designed pipet, after which the gases (in bubble form) are reacted with alkali to remove CO_2. Pyrogallol solution introduced into the syringe then absorbs the O_2. The change in bubble volume is equal to the volume of O_2 present (Ref. 30). See Figure 15 for an illustration of the microgasometric method equipment.

2.83 Advantages and Disadvantages of the Micro-Gasometric Method

The principle advantages of the method are that:

(1) The technique is adaptable to field use.

(2) Simultaneous analysis for O_2 and N_2 are an inherent feature of the method. With some simple procedural modifications CO_2 may also be determined, albeit with much lower accuracy.

(3) A number of substances generally present in polluted waters do not interfere.

However, the method has a number of limitations:

(1) It is not readily adaptable for continuous monitoring type analysis, and

(2) It is not applicable to _in situ_ DO analysis.

2.9 Radiometric Analysis for DO

This method is based on the quantitative oxidation of the radioactive Tl^{204} by oxygen. Tl^{204} is a β-emitter with a 3.6 year half-life. Thus the sensitivity of this method is not greatly affected by a decay period of some months. Figure 16 illustrates the main features of the apparatus employed. It is essentially a column of Cu turnings on which Tl^{204} has been electro-deposited. Two Geiger-Mueller (G-M) flow counters, one preceding, the other following the column, count background and radioactive effluent, respectively.

The solution to be examined for DO is checked by the first G-M counter for background β-radiation, after which it is passed through the column and the eluate checked by the second counter. Oxidation of Tl^{204} takes place on the column, as shown below:

$$(21)\quad 4Tl_{(s)} + O_{2(aq)} + 2H_2O_{(liq)} \rightarrow 4Tl(I)_{(aq)} + 4OH^-_{(aq)}$$

One mg DO liberates 2.56 x 10^{-2} g of Tl^{204}, so that the counting rate and DO concentration are related by means of a proportionality constant.

2.91 Radiometric Method: Merits and Limitations

Merits:

(1) The method may be adapted to continuous monitoring of DO in effluents, and

(2) Instrumentation is relatively simple, although preparation of the column is a fairly complex procedure.

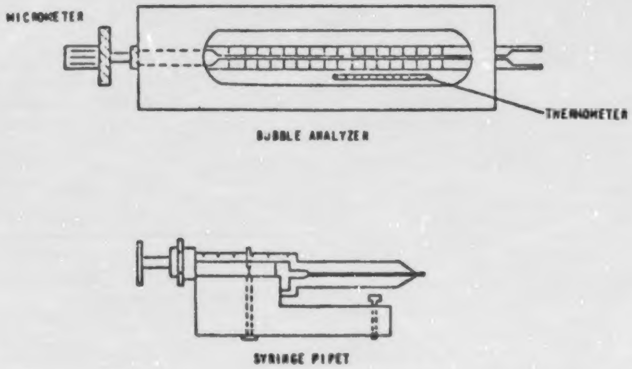

FIGURE 15. *Microgasometric Equipment (from Ref. 6, p. 33).*

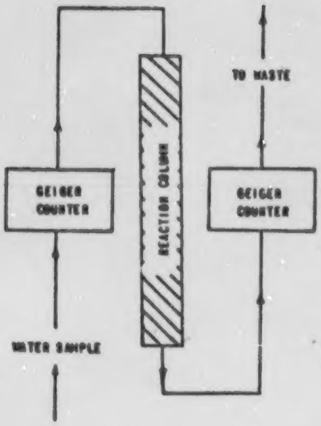

FIGURE 16. Radiometric Apparatus, employing thallium-204 (from Ref. 6, p. 34).

Limitations:

(1) Electrolytes in sea water interfere with the linear response of the G-M counter by affecting the solubility of Tl(I) on the column.

(2) The oxidation reaction Tl → Tl(I) is pH dependent.

(3) Other oxidants interfere markedly at low pH.

(4) With a column of specific activity ∿ 2.0 millicurie (mCi)/gram of Tl, sensitivity is ca. 0.2 mg/l; ie., a solution containing about 0.2 mg/l of oxygen will have a counting rate equal to that of the background counter. Because of the random nature of radioactive decay, a precision of ±2% is about the best one can expect with this method (Ref. 31).

3. Electrochemical Methods of DO Determination

A number of electroanalytic methods have been employed in DO determinations, involving (a) conductimetry, (b) coulometry, and (c) (c) voltammetry (Table 1).

3.1 Conductimetry

The reaction of DO with chemical compounds to form ionic species results in increased conductivity of the solution. The addition of NO to a flowing water sample oxidizes NO as follows:

$$(22)\quad 4NO + O_2 + 2H_2O \rightarrow 4H^+ + 4NO_2^-$$

This reaction increases the ionic strength, μ, of the solution, and consequently, its electrical conductivity. The increase in conductance is directly proportional to the DO concentration of the original sample. Figure 17 depicts the flow diagram of a conductivity apparatus. The water sample is first passed through an ion-exchanger to remove bases and buffer salts which interfere. From there the solution goes through a reference cell to the reaction column where it reacts with the nitric oxide. The oxidation of NO by O_2 is instantaneous (Ref. 32). The treated sample then passes through the second conductivity cell, and the change in DO concentration observed is recorded as [DO].

In another method the anodic corrosion of Pb^{124} or Tl^{126} is utilized to analyse for DO:

$$(23)\quad Pb + O_2 + 2H_2O \rightarrow 2Pb(II) + 4OH^-$$

$$(24)\quad Tl + O_2 + 2H_2O \rightarrow 4Tl(I) + 4OH^-$$

Because OH^- is produced in these reactions, the pH of the solution plays an important part in the above reactions.

With $Tl(OH)_4$ (equivalent conductance 253), 1 mg/l of DO will produce an increase in conductivity of 32 μmhos/cm. Surface waters may

TABLE 1.
(from Ref. 11, p. 324)
Electrochemical Sensors

Type	
a. Conductometric	$L = K_e \sum_i^n C_i \lambda_i z_i$
b. Potentiometric	$E_m = \text{constant} + \frac{RT}{z_i F} \ln \left[a_i + K_j a_j^{z_i/z_j} \right]$
1. Glass electrode	$\text{pH} = -\log a_{\text{H}^+}$
2. Inert metal electrode (redox potential)	$\text{pE} = -\log a_{\text{H}}/(2.3\ RTF^{-1})$
	$\text{Cationic} = \text{pM}^+ = -\log a_{\text{M}^+}$
3. Potentiometric membrane electrodes	$\text{Anionic} = \text{pA}^- = -\log a_{\text{A}^-}$
c. Voltammetric membrane electrodes (dissolved oxygen)	$i_d = \left[zFAP_m \frac{1}{b}\ a_{\text{O}_2} \right]$

L = specific conductance
K_c = cell constant
C_i = ionic concentration
λ_i = ionic equivalent conductance
z_i = ion valency
E_m = measured electrode potential

F = the Faraday constant
K_j = selectivity coefficient
i_d = diffusion current
A = electrode surface area
P_m = membrane permeability coefficient
b = membrane thickness

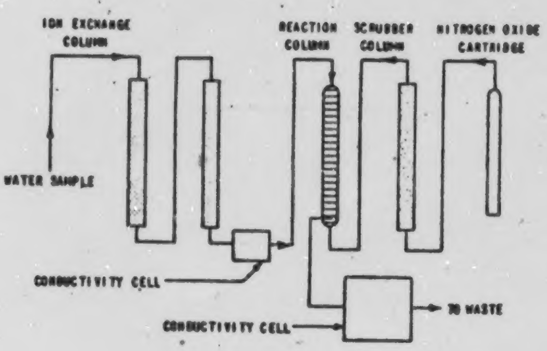

FIGURE 17. Conductivity Apparatus (from Ref. 6, p. 36)

vary in conductivity all the way from 100 to 1000 μmhos.

For minute amounts of DO, the water is first pretreated with ion-exchange resins to attain a pH >7, eliminating interfering carbonates and phosphates and reducing the initial sample conductance. The sample is then passed through the Pb or Tl column and the conductivity change noted. For convenience it is frequently expressed in [DO] units.

3.11 Merits and Demerits of Conductimetry in DO Analysis

The conductimetric method of analysis has been used in boiler water with considerable success. The following are advantages of conductimetry:

(1) The method has a relatively high sensitivity.

(2) Conductimetry may be adapted for continuous monitoring.

However, there are some disadvantages:

(1) The method does not lend itself to in situ monitoring.

(2) In all probability, ion-exchange pretreatment results in some DO loss as a result of reactions between it and the inorganic and organic constituents of the water sample on the large surface area provided by the ion-exchange column.

3.2 Constant Current Coulometric (CCC) Determination of DO

Water that has been saturated with air at 1 atmosphere and 25°C contains 8.18 mg/l of oxygen in solution. This has the appreciable coulometric equivalent of 0.1083 amp sec/g. Of the limited number of coulometric methods discussed in the literature, two have been selected for treatment here, both of which depend on the principle of constant current coulometry (Ref. 33, 34).

3.21 Electrolytic Reduction of Chromic Ions

The sample to be tested is treated with a deoxygenated solution of chromic ion. Chromous ion is generated during electrolysis, followed by the oxidation to Cr(III) by the DO present in solution. The end of the titration is signaled by the appearance of excess chromous ion in solution. Sensitivity of the method is of the order of .03 mg/l (in terms of DO present); accuracy is ±2%.

3.22 Electrolytic Oxidation of $Cu(NH_3)_2^+$

The cuprous-ammonium complex ($Cu[NH_3]_2^+$) is oxidized to the cupric ammonium state ($Cu[NH_3]_2^{++}$) by DO. Advantage is taken of this reaction to determine DO in solution. The oxidation step is followed by back-reduction of the complex to the cuprous state at a Pt cathode. The amount of current passed is a measure of the DO present in the test solution.

3.23 Limitations of CCC Methods

In general, coulometric methods for the analysis of DO (or other constituents) are only applicable to waters of high purity. Under these conditions the methods discussed above are both very accurate and highly sensitive.

3.3 DO Analysis by Voltammetric Methods

These methods depend on the electrolytic reduction of DO at an inert sensing electrode, thereby generating a current which is directly proportional to the (molecular) oxygen present in the solution. The electrode reaction is a function of (a) the nature of the electrode, (b) the pH of the solution, and (c) the imposed potential at the solution-electrode interface.

The usual voltammetric type of system has a large non-polarized* reference electrode and a polarizable micro-electrode, such as the dropping mercury (Hg) electrode. A typical voltammetric circuit is illustrated below (Figure 18). In it, a variable potential is applied to the system, and the current measured by a sensitive galvanometer.

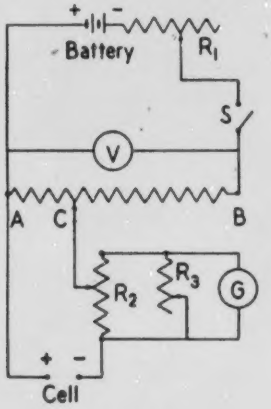

FIGURE 18. Schematic Voltammetric Circuit (from Ref. 39, p. 300).

Current flow at constant voltage is a function of parameters such as (a) the kinetics of the electrochemical reaction, and (b) the rate at which the reactant in question is transported to the electrode. Transfer of reactants may be effected by (1) diffusion, (2) convection, or (3) the migration of charged species. The migration factor may be virtually eliminated by conducting the electrolysis in the presence of a large excess of supporting electrolyte.

Because electrode reactions are generally fast, the concentration of the reactive species over a definite potential range is zero at the electrode surface itself. Under these conditions, the rate of mass transfer, and thus diffusion, becomes the rate-determining factor in the electrolysis.

The diffusion current i_d, of this system is proportional to the DO present. It is possible to obtain reproducible C-V curves provided the same cleaning procedures are maintained throughout the measurements.

A number of other hydrodynamic and diffusion-transport based systems have been described Ref. 36, 37, 38).

3.31 Mechanism of Electrolytic Reduction of Molecular Oxygen

The mechanism of the reduction process for oxygen has been investigated by many workers and is known to depend on the nature and surface properties of the cathode used as well as the pH and ionic strength of the solution. Such processes as the splitting of the molecular O-O bond, adsorption and desorption of O_2 on the electrode surface, and proton transfer, are all involved in the reduction process. In addition, the formation and disappearance of transient oxide films appear to be a factor with some metal electrodes (Ref. 35).

When classified according to the mechanism of mass transfer involved, voltammetric electrode systems fall into three main categories:

(1) Diffusion transport and hydrodynamic systems such as those utilizing a rotating Pt electrode;

(2) Semi-'infinite diffusion' transport systems of the polarographic type, such as the dropping Hg electrode; and

(3) 'Finite diffusion' transport systems exemplified by membrane electrodes.

3.32 The Rotating Platinum Electrode

Systems composed of a rotating electrode, or those utilizing a stationary electrode in a stirred solution belong to class (1) above. Rotating Pt electrodes have been in use for some years in DO analysis. The usual electrode assembly consists of a Pt wire which protrudes several millimeters through the wall of a glass tube. The latter rotates at some constant velocity such as 600 RPM. The bottom of the tube is filled with Hg and electrical contact is established by means of another Pt wire dipped into Hg (see Figure 19 below).

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*A polarized electrode is one that has been forced to maintain a potential different from the equilibrium potential of the solution.

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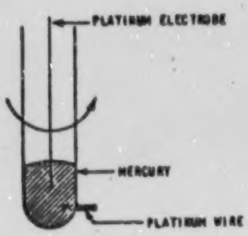


Figure 19. Rotating Platinum Electrode (from Ref. 6, p. 39).

3.33 Applications and Limitations of the Rotating Platinum Electrode

The rotating Pt electrode is usable in:

(1) in situ analysis for DO, and

(2) in the continuous monitoring of "clean" waters.

Limitations of this type of electrode system stem from:

(1) Electrode poisoning by any electroactive and/or surface active substances often present in waters and wastewaters which inhibit or totally interfere with the electrode-oxygen reactions.

(2) Difficulties encountered in obtaining constant speed of Pt electrode rotation, resulting in the distortion of the diffusion curves.

3.4 Polarographic Methods of DO Analysis

Polarography utilizes diffusion transport characteristics in "infinite" media. As such it constitutes a special category under voltammetry. Dropping Hg electrodes have been in use for a very long time to determine DO in water. The method was described in the 11th edition of Standard Methods (Ref. 40) as an alternative (and tentative) procedure when the Winkler method could not be employed -- as, for example, in the presence of high concentrations of industrial wastes. In a typical polarographic cell (Figure 20) a capillary tube attached to a vertical glass tube filled with Hg serves as the cathode. The anode may be a pool of Hg or the standard calomel electrode. A reservoir regulates the height of Hg in the cathode, and with it, the flow rate from the capillary. For DO analyses, a 3-4 second drop time is preferred. The steady supply of drops of Hg result in a continuous renewal of cathode surface. Figure 21 illustrates a typical C-V curve of an oxygen polarogram on Pt, showing the double wave of oxygen.

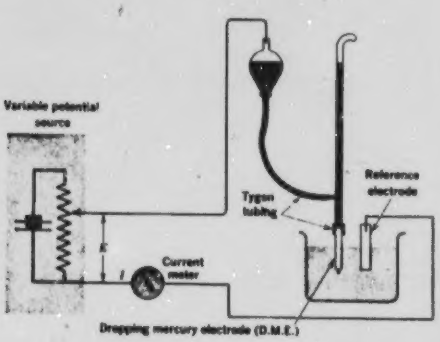

Variable potential source
E
I
Current meter
Tygon tubing
Reference electrode
Dropping mercury electrode (D.M.E.)

Figure 20. Schematic Polarographic Circuit (from Ref. 41, p. 51).

The oxygen content of the solution is related to the diffusion current i_d, by the following equation:

(25) $i_d = 607\ nm^{2/3} t^{1/6} D^{1/2} C$, where

n is the number of electrons participating in the electrode reaction/M of O_2,

m is the flow rate of the Hg in mg/sec

t is the drop time, in seconds,

D is the diffusion coefficient for molecular O_2 in cm^2/sec, and

C is the concentration of DO in mm/l.

Since n, m, t, and D are constant for any fixed system (S), the Ilkovic equation reduces to:

(26) $i_d = \phi C_S$, where

ϕ is the coefficient of sensitivity, in $\mu A/mm^{-1}$, and amperes = A

C_S is the concentration in a particular (fixed) system, S.

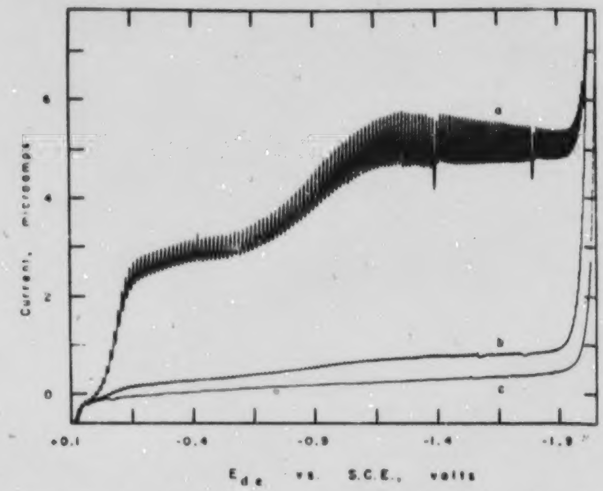


FIGURE 21. Polarograms of 0.1F potassium chloride (a) saturated with air, showing the double wave of oxygen, (b) partially deaerated, and (c) after complete deaeration (from Ref. 42, p. 136).

Instrument calibration is best done with the solution to be analyzed. Figure 22 illustrates a typical plot of the diffusion current in μ ampere compared with a DO determination using the Winkler method.

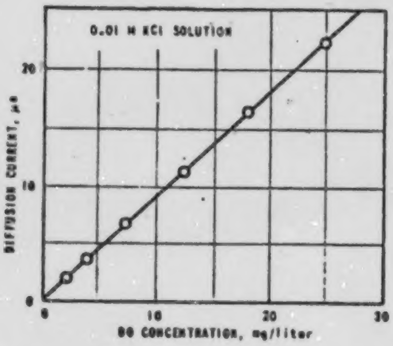


Figure 22. Calibration Curve (from Ref. 6, p. 43).

The selection of operating voltage for diffusion current measurements is important. It must be chosen to avoid interference from contaminants with the O_2 electrode reaction. A preliminary oxygen polarogram of the sample to be analyzed is useful for determining the applied voltage to be employed (Ref. 43).

Anionic surface active agents (surfactants) have been found to interfere with the electrode reaction corresponding to the first wave potential region, whereas cationic surfactants apparently interfere with those electrode reactions corresponding to the second wave potential (see Figures 23 a, b, c).

The use of a voltage corresponding to the second oxygen wave is preferable, since (1) the usual surface active agents present in waste water do not interfere, (2) the need for,the addition of a maximum suppressor (a surfactant) is eliminated, (3) the interferences from the oxidation waves of sulfides and cyanides are eliminated, and (4) higher sensitivity is achieved because of the larger current.

The considerable number of attempts to adapt dropping Hg electrode procedures to the routine analysis of natural and waste waters have been generally unsuccessful because of difficulties encountered in continuous operations, particularly in heavily polluted waters (Ref. 44, 45). The so-called "wide bore" dropping mercury electrodes have had some success (Ref. 46, 47). This modification has an upward

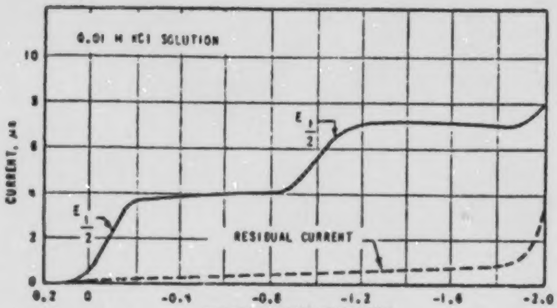


Figure 23 (a). Oxygen polarogram -- no surfactant (from Ref. 6, p. 42).

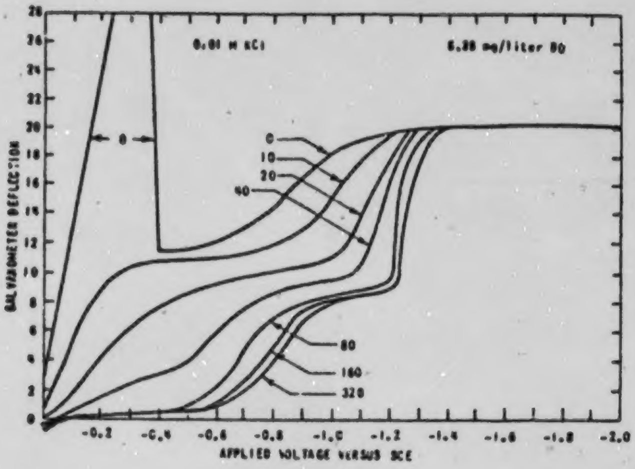


FIGURE 23 (b). Oxygen polarograms at different aerosol O.T. concentrations (mg/liter) (from Ref. 6, p.44).

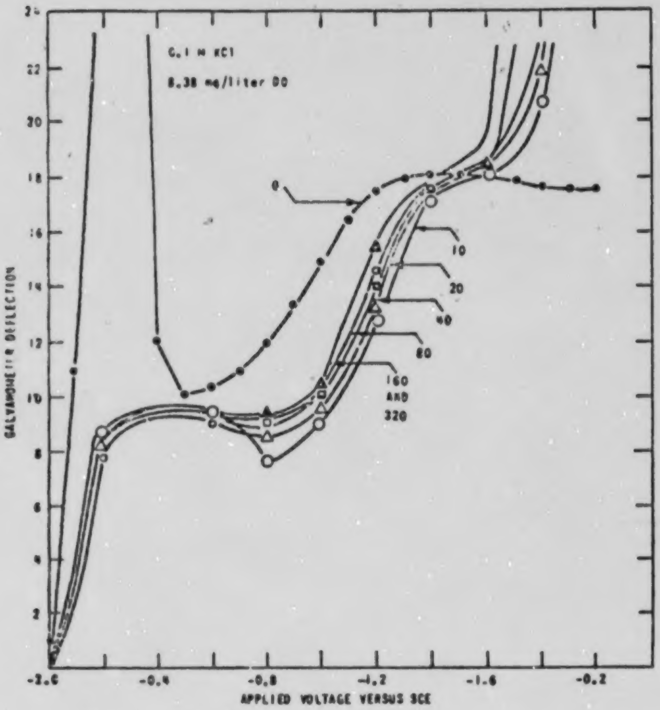
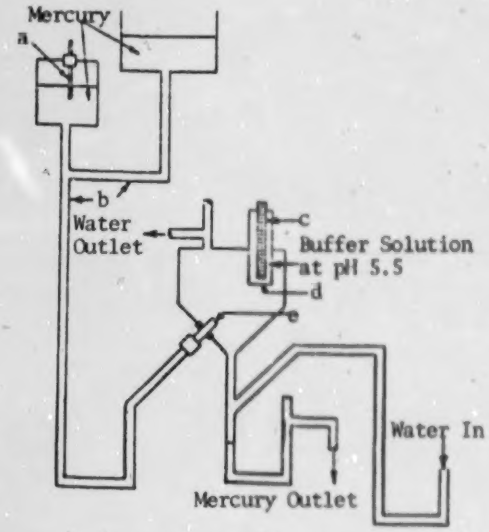


FIGURE 23 (c). Oxygen polarograms at different Roccal concentrations (mg/liter) (from Ref. 6, p. 45).

sloping capillary with an I.D. of 0.8 mm, and a Zn anode (Figure 24). The Hg flow rate is adjusted to about 7 mg/sec with a drop time of 0.2 to 0.3 seconds.



a = Platinum contact

b = Silicon Rubber Tubing

c = Zinc Electrode

d = No. 4 Sintered Glass Disc

e = Dropping-Hg Electrode

FIGURE 24. Rapid-dropping mercury electrode (from Ref. 6, p. 47).

3.41 Advantages and Limitations of Polarography for DO Analysis

The disadvantages of the small bore dropping Hg electrode have already been discussed under section 3.4. The reader is referred to the following additional references for information: References 48, 49.

Rapid dropping Hg electrodes have the following advantages:

(1) Their use minimizes the deleterious effects of surfactants on electrode reactions.

(2) They can be used with either ambient or stationary aqueous solutions.

(3) The nearly 10-fold increase in current in the short drop-time systems results in a considerable increase in sensitivity.

The limitations of polarography for DO analysis of natural and waste waters include:

(1) A lack of ruggedness and portability necessary in field instruments,

(2) Since the polarographic sensing electrode comes into direct contact with the solution, it is subject to the serious interference effects already discussed under 3.4.

(3) Toxicity of Hg to biological systems precludes polarography for respiration and/or oxygen uptake studies†.

The polarographic procedure used strongly influences the accuracy achieved. When interferences are absent, accuracy lies somewhere between 0.05 and 0.10 mg/l, with a precision of ±0.01 mg/l.

3.5 Galvanic Methods of DO Determination

Oxygen-sensitive galvanic cells have a long history. Prior to the invention of the Leclanche dry battery, cells using atmospheric oxygen were employed as sources of electrical energy. The traditional air cell consists of Zn anode(s) and a porous cathode immersed in a 20% sodium hydroxide solution. Unlike the Leclanche cell, the air cell participates conspicuously in the cell reaction, the cell eventually dying as the electrolyte is exhausted.

Special air cells have been designed in which the generated current is proportional to the $[O_2]$ which is in contact with the cathode (Ref. 50, 51, 52). Typical of these analyzers is that used by Hartmann and Braun (Figure 25) which was especially designed for the determination of DO. It employs a small circular Au or Pt cathode and a large area Zn anode which are dipped in a rapidly flowing stream of the test sample. (The stream velocity is maintained at 1 m /sec.) The electrodes are cleaned periodically by rotation against a scraper.

Since changes in conductivity affect DO measurements, a number of circuits have been designed which may be adjusted for variations in conductivity. For low conductivity water, gases such as CO_2, NH_3 and gaseous amines are added to increase the conductivity.

Galvanic methods for DO analysis have been in use for about 40 years. A number of different galvanic systems employing cathodes

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†Waste mercury from laboratory uses is generally collected and reclaimed for economic reasons. The problem of Hg pollution is treated in the metals section of this Volume.

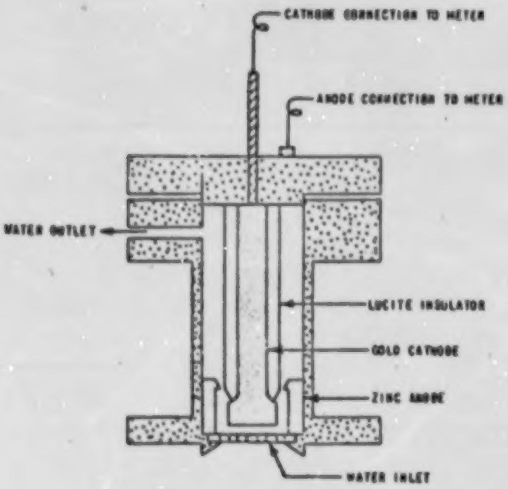


FIGURE 25. Hartmann and Braun Dissolved Oxygen Analyzer (from Ref. 6, p. 48).

of C, Au, or Pt have been used in Europe. Because these cells are susceptible to poisoning by their direct contact with the sample solution, they are of limited application. One method employed to avoid cathode incrustation in waste water analysis has been the addition of HCl to the water sample, using a dosing arrangement preceding the cell itself (Ref. 53).

3.51 Advantages and Disadvantages of Galvanic Methods of DO Analysis

(1) Galvanic methods are adaptable for in situ measurement in flowing streams.

(2) Galvanic methods may be employed in continuous-monitoring systems. However:

(a) Because the sensing element comes into direct contact with the test solution, the cathodes of galvanic cells are subject to poisoning by impurities which may adsorb on the cathode surface or react with the cathode material.

(b) Since the galvanic type analyzer is affected by changes in conductivity, any conductivity change experienced by a stream or estuary will affect the sensitivity of the galvanic cell.

3.6 Membrane Electrodes (ME) in DO Analysis

It is only within the last ten years or so that membrane electrode cells have been developed to a point where they can be of use in environmental monitoring of natural and waste waters. Those systems employed in DO analyses are electrochemical cells of the finite-diffusion type. The principle involved in their operation may best be understood by briefly examining the predecessor of these membrane systems - namely, polarography.

In polarographic-type cells the rate of diffusion of the active species is the sole determinant of the diffusion current. Since the volume of test solution is not fixed, the system is one in which the transport of active species may be viewed as occurring by a semi-infinite diffusion process.

Membrane electrode systems differ in that the diffusion current now depends only on the diffusion rate of the active species in a finite layer of the solution. This condition results from the use of a plastic membrane in close proximity to the electrode surface, thereby effectively separating the bulk of the test solution from the electrodes. Under these conditions the intervening membrane between solution and electrodes may be viewed as a strictly defined diffusion layer. As such its thickness will be independent of the hydrodynamic properties of the solution as a whole. In consequence, membrane electrode systems have more stable characteristics than those exhibited by the conventional polarographic systems.

3.61 Types of Membrane Electrode (ME) Systems

Finite diffusion type electrode systems fall into two main categories: (1) galvanic membrane electrode cells, and (2) voltammetric membrane electrode cells. These differ primarily in that galvanic systems generate their own EMF with the ion species to be analyzed involved as a reactant at one of the electrodes, whereas voltammetric membrane systems are driven by the external application of voltage thereby polarizing the indicator electrode. In this respect, voltammetric membranes resemble conventional polarography.

Descriptions of several systems developed for DO analysis may be found in References 54 and 55.

Mancy and coworkers have reported the successful use of a galvanic membrane electrode type probe in both waste treatment operations and in water pollution control programs (Ref. 56, 57, 58, 59).

The cell consists of a Pb-Ag couple. The lead anode is arranged annularly as shown in Figure 26. A disc shaped Ag cathode is located inside the anode. The couple is then fitted into a plastic collar and the tip of the assembly is covered by a polyethylene membrane between 0.5-1.0 mil in thickness. A small disc of lens paper between the membrane and the electrode tip saturated with 4M KOH, serves as the electrolyte. The system is disassembled periodically for cleaning the electrode surfaces, replenishing supporting electrolyte and replacing the plastic membrane with a new one.

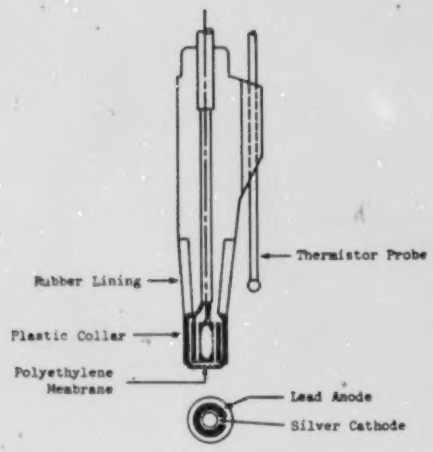


FIGURE 26. Galvanic Cell Oxygen Analyzer (from Ref. 21, p. 280).

The circuitry involved in galvanic sensor systems is relatively simple, requiring only a low impedance galvanometer or microammeter, and, if a recorder is desired, an inexpensive galvanometer-type recorder is generally adequate. Or, a known resistor may be used in the cell circuit and the potential drop then fed to a potentiometer-type recorder. It is a relatively simple matter to include such auxiliary equipment as an alarm, an integrator, or additional control equipment.

Sensitivity of the membrane electrode is not appreciably affected by the load resistance of the circuit because of the large polarization resistance of the sensing electrode with which it is in series. However, the current may be affected at high values of external load.

Johnson and coworkers have described a steam sterilizable galvanic membrane electrode which has been successfully employed in DO determinations in aerobic fermentation units (Ref. 60). The system consists of a Pb-Ag couple, with an acetate-buffer for the supporting electrode.

Galvanic type ME systems, in addition to being self-energized, are self-zeroing, which is advantageous. Voltammetric membrane systems, on the other hand, may exhibit background signals for either sign of an impressed voltage.

3.62 Principles of Oxygen Membrane Electrodes

Oxygen membrane electrodes operate in three principal stages:

(1) Molecular O_2 from the test solution permeates and diffuses through the membrane layer. This is a relatively slow process.

(2) The molecular oxygen then transfers through the electrolyte layer which is in contact with the electrode surface.

(3) Oxygen is electrolytically discharged at the Ag cathode, generating an equivalent amount of current.

In clarifying the principles involved in the oxygen membrane electrode, the reasonable assumption is made that the current generated involves linear finite diffusion only; e.g., the current is solely dependent on the rate of passage of the oxygen through the membrane to the surface of the electrode. This rate is in turn proportional to the oxygen concentration in the water in contact with the membrane. When the cell circuit is initially closed, the current will attain a maximum value representing the charging of the double layer's capacitance. Thereafter, there will be a diminution of current with time, the current-time curve now reflecting the mass transport rate of oxygen (Figure 27). The set of concentration profiles shown in Figure 28 illustrates the change in concentration of electroactive species with time in a cell of electrolyte film thickness A, and membrane thickness B. Measurement of the current at any time t, corrected for capacitance current, depends only on the concentration of electroactive species in the electrolyte film layer.

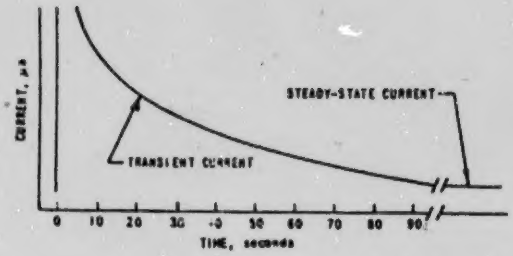


FIGURE 27. Current-Time Curve (from Ref. 6, p. 53).

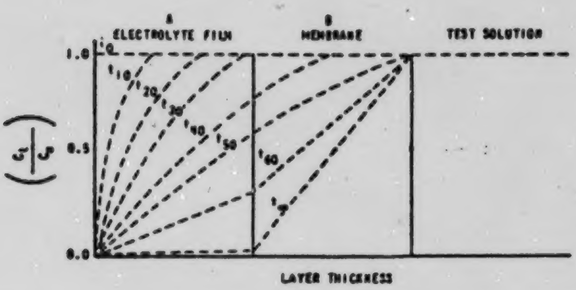


FIGURE 28. Concentration Profiles (from Ref. 6, p. 52).

For large values of t, where a steady state is attained, the following simplified expression holds for the oxygen membrane electrode:

(27) $i_\infty = nF\bar{a}\,\frac{Pm}{B}\,C$, where

n is the number of electrons exchanged per mole of reactant,

F is the Faraday constant (96,500 coulombs),

$\bar{a}$ is the surface area of the indicator electrode,

Pm is the membrane permeability coefficient (in cm^2/sec),

B is the membrane thickness, and

C the concentration of reacting species in moles/cc.

Here the rate-determining factor is transport of the active species through the membrane. Therefore, the current generated will be proportional to the rate at which molecular oxygen permeates the membrane. This depends on the oxygen dissolved in the test solution. Figure 29 illustrates a typical DO vs current calibration curve.

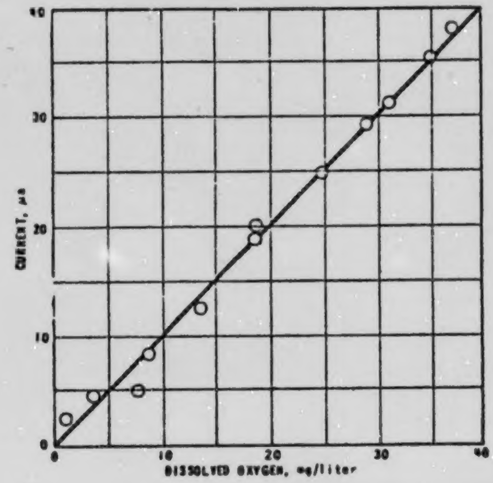


FIGURE 29. Calibration Curve at 25°C (from Ref. 6, p. 54).

The electrode reactions of the galvanic cell oxygen analyzer are as follows:

(a) Cathode reaction:

$$1/2\ O_2 + H_2O + 2e \rightarrow 2OH^-$$

(b) Anode reaction:

$$Pb + 2OH^- \rightarrow PbO + H_2O + 2e$$

(c) Overall cell reaction:

$$Pb + 1/2\ O_2 \rightarrow PbO$$

Although OH^- ions do not appear to be consumed in the overall cell reaction above, they are necessary in order to sustain the anode reaction. Therefore, there will be a deficiency of OH^- at the anode and an increase in OH^- in the electrolyte layer immediately adjacent to the central cathode and radiating toward the periphery of the anode.

For a more detailed treatment of oxygen membrane electrodes as a "2-film" system, the reader is referred to Reference 6, p. 51.

3.63 DO Probes: Some General Considerations

Oxygen membrane electrodes have three components: the membrane, the sensing element, and the electrolyte. Of these, the membrane is the unique feature of the system and has three separate functions:

(1) It acts as a protective barrier between the solution to be tested and the sensing element.

(2) It enables the supporting electrolyte to maintain contact with the electrodes.

(3) It constitutes a finite diffusion layer, with a thickness which is independent of the hydrodynamic properties of the solution bo be analyzed.

In order to qualify for use in a DO probe, a membrane:

(1) should have excellent oxygen permeability whilst remaining essentially impermeable to other species of the solution tested;

(2) should have permeability characteristics which are constant with time, and inert to the constituents of test solutions, and

(3) the membrane in question should be sufficiently resistant to tearing and/or breakage to enable one to apply it with ease to the electrode surface.

The following materials have shown good permeability characteristics for oxygen: polyethylene, polypropylene, synthetic rubber and teflon. In particular, polyethylene membranes which have low crystallinity show exceptional O_2 permeability (Ref. 61).

While Pt has been extensively employed as a sensing element for O_2, Mancy et al (Ref. 58) have found that Au and Ag also have merit as cathodes for O_2 detection.

Electrolyte solutions in ME systems must be highly conducting aqueous solutions which do not affect the electrodes. For voltammetric systems, the nature of the electrolyte and its concentration is dictated by the reference anode. For example, with an Ag/AgCl reference electrode, the electrolyte of choice would be a 3% KCl solution.

3.64 Performance Characteristics of DO Probes

Figure 29 shows a typical calibration curve for a membrane oxygen electrode, in terms of the standard Winkler test.

For proper operation of the ME there must be adequate mixing in the test solution which is in contact with the analyzer tip. This is achieved in the laboratory by magnetic or motor-driven glass stirrers. In the field this movement may be provided by the natural stream flow, by towing the probe behind a vessel, or by manual up and down movement of the probe. In another method which has been employed, attachments with small battery-driven propellers are mounted on the tip of the probe to achieve the necessary movement.

The importance of stirring to obtaining maximum sensitivity in the DO probe is evident from Figure 30.

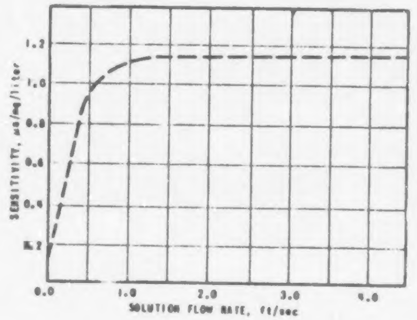


FIGURE 30. Effect of stirring on sensitivity (from Ref. 21, p. 286).

3.65 Temperature Coefficients of DO Probes

Voltammetric membrane electrodes have relatively high temperature coefficients (Figure 31), chiefly because of alterations in membrane permeabilities with changes in temperature. Electrode reaction kinetics and electrode potentials are essentially temperature independent, however,

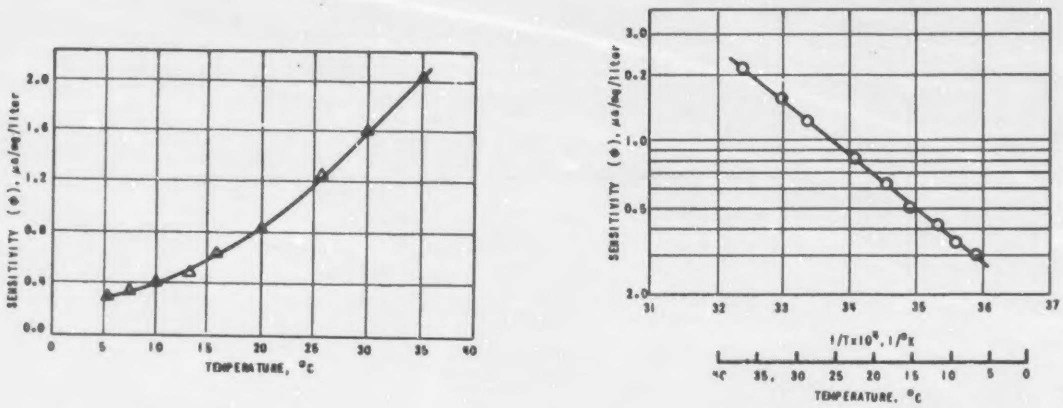


FIGURE 31 (a). Effect of temperature on sensitivity (from Ref. 21, p. 288).

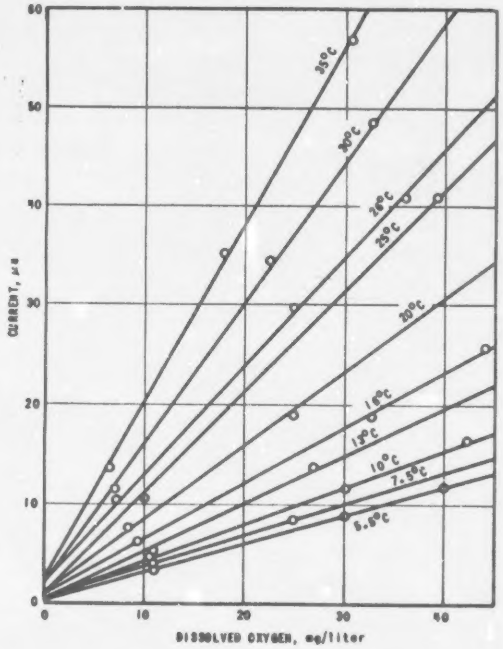


FIGURE 31 (b). Calibration curves for different temperatures (from Ref. 21, p. 287).

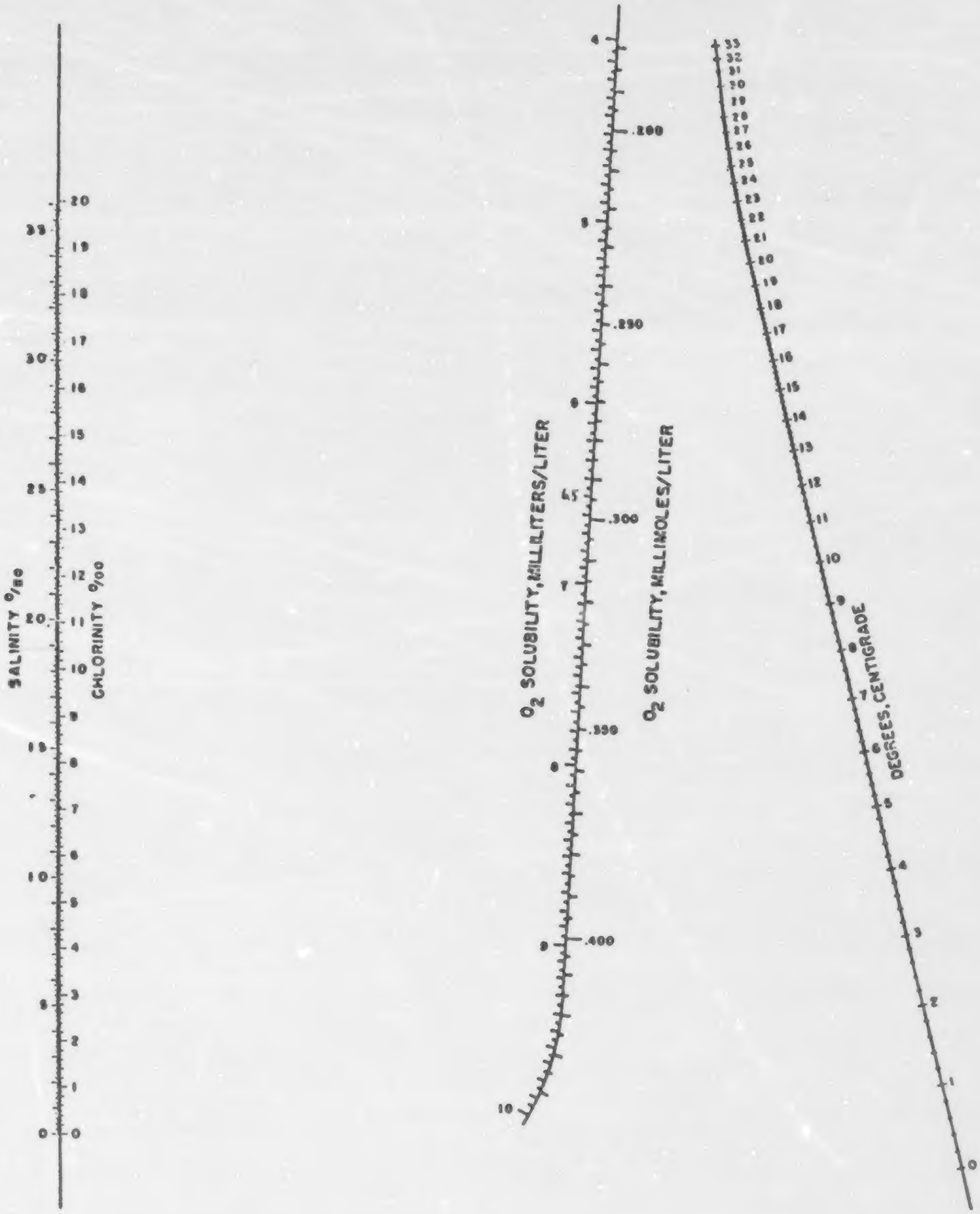


FIGURE 32. Oxygen solubility nomograph for seawater with respect to an atmosphere of 20.94% oxygen and 100% relative humidity. Prepared by William Gilbert, Department of Oceanography, O.S.U. Corvallis, Oregon 97331 (June 1967). (From Ref. 65).

The variation of sensitivity of DO probes with temperature is expressed by the equation:

$$(28) \quad \frac{d\phi}{dT} = m^\circ \frac{\phi}{T^2}, \text{ where}$$

d is the sensitivity in μA/mg/l

T is the temperature, expressed in °K, and

m° is the temperature coefficient in °K.

A plot of log ϕ vs 1/T is linear with a slope equal to $-m^\circ/2.303$ and an intercept b:

$$(29) \quad \text{Log } \phi = -\frac{m^\circ}{2.303}\frac{1}{T} + b$$

Once m° has been determined, it is possible to calculate the instrument sensitivity at any desired temperature (Ref. 58). Nomographic temperature correction charts may be constructed (Figure 32). These calibrated charts should be used when high accuracy is desired. For lesser accuracy, ME systems with a thermistor setting incorporated in the circuit may be used (Ref. 64).

3.66 Interpretation of Data Obtained from ME Systems

An examination of the similarities between glass membrane electrodes used in measurement of pH, and pNa, and oxygen membrane electrodes may be illuminating.

In glass electrode systems, the asymmetry potential across the membrane is directly related to hydrogen ion activity. Similarly, in oxygen ME systems, the measured diffusion current is a function of the difference in chemical potential across the membrane of the reactive species. Thus both systems measure intensive properties of the solutions rather than extensive ones, such as those measured in a Winkler titration, or the titration of an acid with a standard alkaline solution. The values of the diffusion currents obtained from ME systems will be a linear function of concentration under ideal conditions only. The real diffusion equation for ME's is more correctly written:

$$(30) \quad i = (nF\bar{a}\,\frac{Pm}{B})a = \phi_a a = \phi_a \gamma C, \text{ where}$$

ϕ_a is a sensitivity coefficient related to activity and expressed in μA/mole/cc,

γ is the activity coefficient of molecular oxygen,

n is the number of electrons exchanged/mole of reactant,

F is the Faraday constant (96,500 coulombs),

$\bar{a}$ is the surface area of the indicating electrode, in cm^2

B is the membrane layer thickness in cm,

Pm is the membrane permeability coefficient in cm^2/sec,

a is the activity of molecular oxygen in moles/cc, and

C is the concentration of molecular oxygen in moles/cc

Diffusion current depends on ionic strength of the solution:

$$(31) \quad i = (e^{K_s I} \phi_a)C, \text{ where}$$

K_s is a salting-out coefficient and I the ionic strength of the solution. The above equation correlates diffusion current with the molecular oxygen concentration in solution; the latter is a function of ionic strength. For distilled water I = 0, and

$$e^{K_s I} = 1.$$

Therefore, equation (31) reduces to equation (30). By means of the last two equations, one can determine the important activity coefficients, γ, and salting-out coefficients, K_s, in salt solutions such as $CaCl_2$, XCl, and Na_2SO_4. Figure 33 correlates the sensitivity ϕ_a with ionic strength.

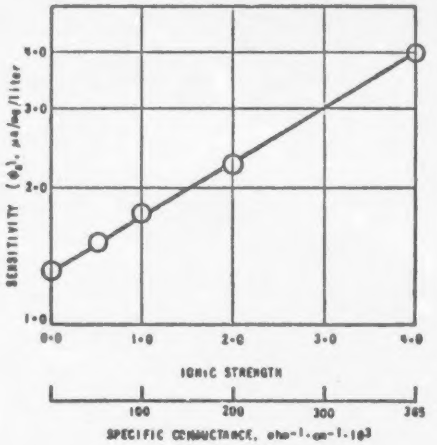


FIGURE 33. Effect of ionic strength on sensitivity (from Ref. 6, p. 60).

It has been shown that the temperature and salt effects in ME systems may be compensated. The effect of temperature may be expressed as:

$$(32)\quad i = \phi_{o,t} e^{-\frac{E_p}{R}\Delta\frac{1}{T}} C, \text{ where}$$

$\phi_{o,t}$ is the sensitivity (current, amperes; DO concentration moles/1) at a reference state, with respect to t in °C,

E_p is the activation energy for membrane permeation (cal/mole),

T is the temperature in °K,

R is the gas constant (cal/mole/°K), and

C is the molecular oxygen concentration in moles/1.

The corresponding salt effect on sensitivity is:

$$(33)\quad i = \phi_{o,s}\, e^{K_s \Delta I} C, \text{ where}$$

$\phi_{o,s}$ is the sensitivity at a reference state with respect to the ionic strength of the solution (units: amp/mole/1).

The ionic strength, μ, of any solution may be accurately determined from conductance measurements:

$$(34)\quad L = \Theta + \lambda I - \delta I^2 + \Gamma I^3, \text{ where}$$

L is the specific conductance in $\text{ohm}^{-1}\text{cm}^{-1}$; and Θ, λ, δ, and Γ are constants. The nonlinear expression above may be approximated by:

$$(35)\quad \Delta L = K_i\, \Delta I, \text{ where}$$

K_i is a proportionality constant.

This approximately linear relationship of conductance to ionic strength holds in most surface waters, including estuaries, but fails for industrial waste waters with high salt concentrations. Combining equations (33) and (35), we obtain

$$(36)\quad i = \phi_{o,s} e^{K'_s \Delta L} C, \text{ where}$$

$K'_s = K_s K_i$.

The exponential terms in equations (33) and (36) reflect temperature and ionic strength effects, respectively. It is possible to compensate for these effects to some extent by employing the electronic compensator diagrammed in Figure 34.

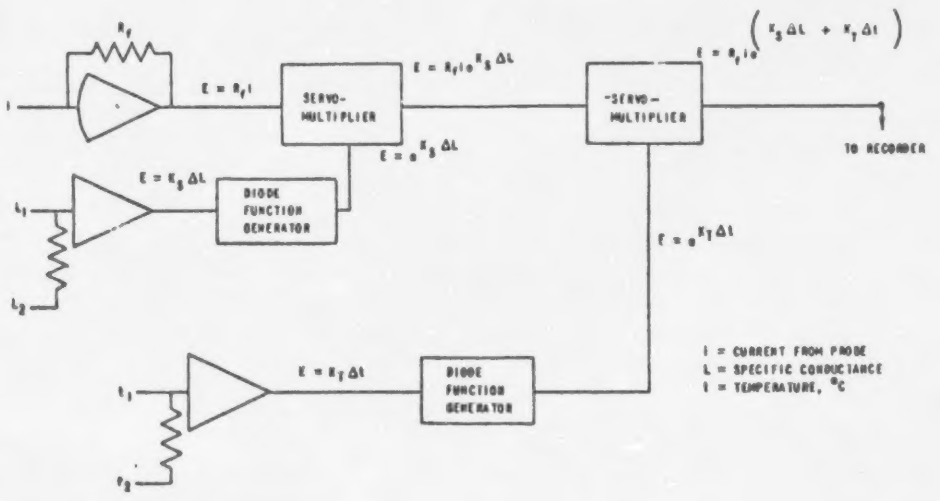
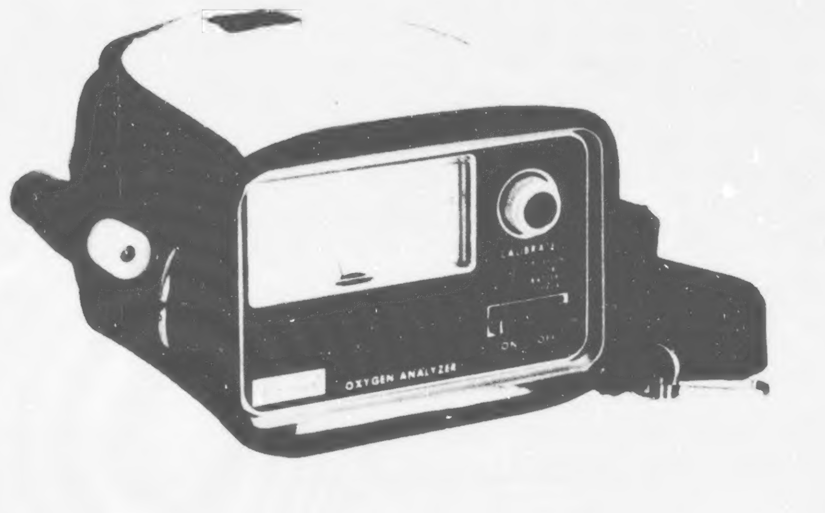


FIGURE 34. Compensator for temperature and salinity (from Ref. 6, p. 63).

Portable Oxygen Analyzer

Edmont Wilson Model 60-620



Class	Continuous/Portable
Categories of Water	Fresh/Waste
Principle of Operation	The analyzer consists of a gold cathode, silver anode, temperature compensating thermistor, a source of polarizing voltage and a readout. The electrodes are connected by means of a conductive gel of cellulose-base containing potassium chloride. They are separated from the gas or liquid sample by a semi-permeable Teflon membrane which shields the electrodes from contamination. When a potential of 0.8 volts is applied between the electrodes, oxygen (O_2) passing through the membrane is reduced at the cathode, generating a current, the magnitude of which is proportional to the amount of oxygen present. Since the diffusion rate of oxygen passing through the membrane increases with increasing temperature the instrument is equipped with a thermistor (resistance thermometer) which compensates for changes in temperature. Temperature changes between 59-122°F are thus automatically compensated to within ~2% of the reading indicated. Electrode Reactions: Anode: $2Ag + 2Cl^- \rightarrow 2AgCl + 2e$ Cathode: $1/2O_2 + H_2O + 2e \rightarrow 2OH^-$ Sensitivity of the sensor is reduced in water by virtue of the increased effective thickness of the Teflon membrane, due to an adsorbed film of water. This increases the distance which O_2 must traverse to the electrode. Diffusion of O_2 in liquids is so much slower than in gases, that the sensor must be in motion in order to replenish even the minute quantity of O_2 consumed by the sensor.
Minimum Detectable Sensitivity	0.1% O_2
Range	0-25% oxygen

3.67 Merits of ME Systems

(1) Molecular oxygen activity and concentration can be determined with ME systems. Activity measurements are of particular interest where one is concerned with making environmental measurements or in the examination of biochemical systems.

(2) Because of the presence of the membrane in ME systems, analysis is feasible in contaminated water samples containing ionized salts and organics.

(3) The ability of the membrane to function as a diffusion layer independent of hydrodynamic properties in the main body of the test solution results in more stable performance of ME systems in flowing conditions, compared with other electrode systems.

(4) ME systems are uniquely qualified for measuring DO in a variety of states from aqueous and non-aqueous solutions to the gas phase.

(5) ME systems are uniquely suited to field measurement; they are rugged, portable, easy to operate and maintain, and are ideal for the measurement of DO under adverse conditions.

(6) ME systems are completely submersible, and they may be adapted for measuring DO _in situ_, sometimes at great depths.

(7) ME systems, in common with other electrochemical systems, can be used in continuous monitoring.

3.68 Some Limitations of ME Systems

The procedures used in ME-DO analyses are generally quite simple. Nevertheless, a number of difficulties have been encountered:

(1) One of these probably results from a lack of knowledge of the fundamental principles involved in the successful operation of ME's. Because there is no continual renewal of ME surface (as is the case in polarographic analyses), adequate renewal of the active species at the electrode must be insured by the stirring or other means of motion provided. An inadequate flow across the surface of the membrane will result in erratic response. It is therefore essential to maintain a threshold mixing value in the solution.

(2) It is possible to contaminate the sensing element during recharging, and considerable care must be exercised to avoid this pitfall.

(3) Other gases which are reduced at the potential of the sensor, such as the halogens, or SO_2, may cause erroneous readings if they permeate the selective membrane. Fortunately, these are rarely present in the free state in the samples tested. CO_2 and H_2S are other potential contaminants; they interfere either by reaction with the electrolyte, or by poisoning the sensing element.

3.69 Some Applications of Oxygen Membrane Electrodes

Oxygen sensors of the ME type have already been widely employed in the environmental field for such applications as the monitoring of lakes and rivers, studies concerned with DO consumption in domestic sewage, and a number of aeration studies (Ref. 57, 59, 67).

Oxygen ME's have also been employed in studies involving fermentation processes (Ref. 68), the continuous monitoring of activated sludge processes, a number of oceanographic investigations (Ref. 70, 71), and as a substitute for the Warburg gas apparatus.

4. Some Suggested DO Criteria for Natural Waters

The following recommendations were made by the National Technical Advisory Committee with regard to the preservation of native biota (Ref. 72):

(1) For a diversified warm-water biota, including game fish, DO concentration should be above 5 mg/1, assuming normal seasonal and daily variations are above this concentration. Under extreme conditions, however, they may range between 5 and 4 mg/1 for short periods during any 24-hour period, provided that the water quality is favorable in all other respects. In stratified lakes, the DO requirements may not apply to the hypolimnion. In shallow unstratified lakes, they should apply to the entire circulation water mass.

These requirements should apply to all waters except administratively established mixing zones. In lakes, such zones must be restricted so as to limit the effect on the biota. In streams, there must be adequate and safe passageways for migrating forms. These must be extensive enough so that the majority of plankton and other drifting organisms are protected (see sections on zones of passage).

(2) For the cold-water biota, it is desirable that DO concentrations be at or near saturation. This is especially important in spawning areas where DO levels must not be be below 7 mg/l at any time. For good growth and the general well-being of trout, salmon, and their associated biota, DO concentrations should not be below 6 mg/l. Under extreme conditions, they may range between 6 and 5 mg/l for short periods provided the water quality is favorable in all other respects and normal daily and seasonal fluctuations occur. In large streams that have some stratification or that serve principally as migratory routes, DO levels may range between 4 and 5 mg/l for periods up to 6 hours, but should never be below 4 mg/l at any time or place.

(3) DO levels in the hypolimnion of oligotrophic small inland lakes and in large lakes should not be lowered below 6 mg/l at any time due to the addition of oxygen-demanding waste or other materials.

The EPA has issued an updated compilation of Federal/State criteria for dissolved oxygen. Because of the difference in criteria from one state or territory to another, the reader is referred to the original digest for information on DO criteria of the individual states (Ref. 73).

5. Summary and Conclusions

Dissolved oxygen has long been recognized as an important parameter for the measurement of water quality. Until quite recently the methods of DO determination were largely wet-chemical, the Winkler procedure and its variants being the method of choice in most laboratories concerned with water quality measurement. However, wet-chemical methods of DO analysis, while sensitive, suffer from two major disadvantages:

1) They are relatively slow and not suited to on-line monitoring.

2) They may not reflect accurately the in-stream conditions at the precise time of sampling.

The development of DO sensors within the past ten years has kept reasonable pace with the demands of the growing environmental market. There is now a plethora of DO sensors available, some of which are designed for continuous on-line monitoring. Most are intended for in-stream or in situ use, and the portable varieties are the instruments of choice for field work. However, it is important to recognize that the proper maintenance and calibration of field instruments is necessary to insure their reliability.

The National Oceanographic Instrumentation Center is engaged in a long-term study concerned with the evaluation of DO sensors. To date, one detailed evaluation of five sensors presently in use has been published (Ref. 74). Another such survey has been initiated, but is still in the early stages (Ref. 75). Public water quality control laboratories, such as those administered by the California Regional Water Quality Control Board and the EPA have occasionally carried out independent evaluations of instruments for specific uses. It would be desirable to have more of these studies published in the open literature to avoid duplication of effort and the obvious logistic difficulties faced by the individual user attempting to make the best choice for a specific purpose.

The sensors presently available can vary quite widely in such characteristics as temperature sensitivity, flow sensitivity, effect of depth, stability and response characteristics, ease of recharging with electrolytes and replacing of membranes, useful life of replaceable parts, and initial and replacement costs.

There is still sufficient room for improvement in the areas of flow sensitivity, temperature-compensated direct read-out type instruments, and the development of membranes with imporved characteristics and specificities to warrant a considerable research effort in these areas.

In the following instrument notes we shall address outselves to these questions of performance and characteristics insofar as the information is presently available. It is to be hoped that the potential user of DO probes will find these notes of considerable help in locating those instruments best adapted to fill the specific demands of a particular job, thereby narrowing the field to a point where the selection of an appropriate sensor becomes a less confusing and frustrating experience.

6. Acknowledgments

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72. Water Quality Criteria, Report of the National Technical Advisory Committee to the Secretary of the Interior, U.S. Government Printing Office, Washington, DC (April 1, 1968).

73. Water Quality Standards Criteria Digest. A Compilation of Federal/State Criteria Dissolved Oxygen, EPA, Washington, DC (Aug. 1972).

74. Barbara S. Pijanowski, "A Quantitative Evaluation of Dissolved Oxygen Instrumentation," AIAA Paper no. 71-1053, Joint Conference on Sensing Environmental Pollutants, Palo Alto, CA (Nov. 8-10, 1971).

75. Private communication from Barbara S. Pijanowski, NOAA, Washington, DC.

8. Appendix: Notation

A = Amperes; also thickness of the electrolyte solution film, cm

a = Activity, molar units

$\bar{a}$ = Surface area of indicator electrode, cm^2

B = Thickness of the membrane layer, cm

C = Concentration of dissolved oxygen, moles/liter

C_s = Salt concentration, mg/liter

D = Diffusivity coefficient, cm^2/sec

E_m = Measured electrode potential, V

E_o = Standard electrode potential, V

E_p = Activation energy of permeation of membrane, cal/mole

F = The Faraday (96,500 coulombs)

G = Free energy

$\bar{g}$ = Acceleration, cm/sec^2

g = Weight in grams

H = Henry's Law constant, 5.89×10^5 mm Hg/mole/liter

h = Depth (cm)

I = Ionic strength

i = Current, A

i_d = Diffusion current, A

J = Flux of molecular oxygen, $moles/cm^2$-sec

K_i = Conductance proportionality constant

K_s = Salting-out coefficient

K'_s = Modified salting-out coefficient

L = Specific conductance, $ohm^{-1}cm^{-1}$

M = Molecular weight, g/mole

m = Rate of flow of mercury, mg/sec

m° = Temperature coefficient, °K

n = Number of electrons transferred per mole in redox

N_i = Number of gram moles of solute

P = Partial pressure of oxygen, 154 mm Hg at sea level

P_m = Permeability coefficient, cm^2/sec

q = Number of coulombs passed in electrolysis

R = Gas constant = 0.0821 L -atm/mole/°K = 1.99 cal/mole°

S = Oxygen solubility, mg/liter

S_o = Oxygen solubility in distilled water, mg/liter

T = Absolute temperature, °K

T_c = Temperature, °C

t = Time

V = Volume

v = Velocity of molecular oxygen, cm/sec

$\bar{v}$ = Partial molal volume of solute, liter/atm

X = Mole fraction

x = Distance, cm

Z = Ionic charge

α = Constant

β = Constant

Γ = Constant

λ = Constant

δ = Constant

γ = Activity coefficient

ρ = Density of solution, g/cm^3

ΔH = Heat of solution, cal/mole

Ψ = Electrostatic charge

μ = Chemical potential, cal/mole also μ = micro

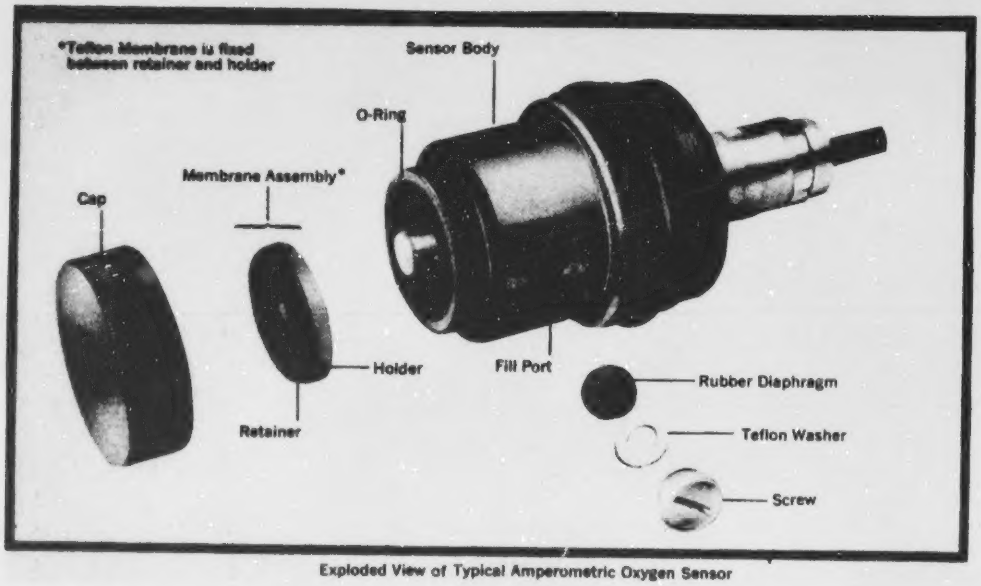
$\bar{\mu}$ = Electrochemical potential

θ = Constant

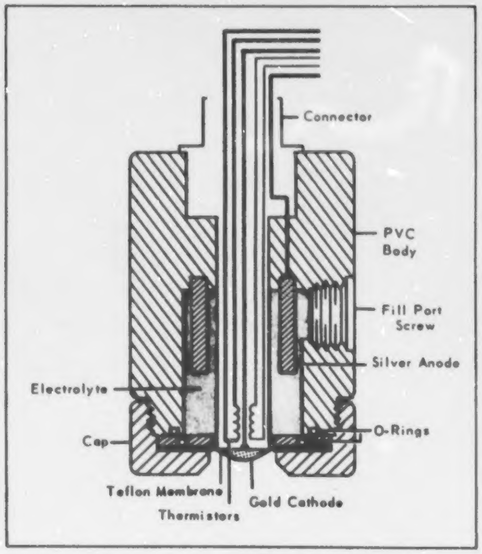
ϕ = Sensitivity coefficient, μA per unit concentration

Dissolved Oxygen Analyzer

Beckman Model 735, Catalog No. 191600


*Teflon Membrane is fixed between retainer and holder
Sensor Body
O-Ring
Membrane Assembly*
Cap
Holder
Fill Port
Rubber Diaphragm
Retainer
Teflon Washer
Screw

Exploded View of Typical Amperometric Oxygen Sensor


Connector
PVC Body
Fill Port Screw
Silver Anode
Electrolyte
O-Rings
Cap
Teflon Membrane
Gold Cathode
Thermistors

Amperometric Oxygen Sensor

Class	Continuous-Sensor, Laboratory/Field
Categories of Water	Fresh or Waste (May be used in salt water by use of correction factors for oxygen solubility)
Principle of Operation	Polarographic oxygen sensor with a large silver anode and gold cathode; electrodes are protected from the solution by a thin Teflon membrane. An aqueous KCl solution confined by the membrane serves as the electrolyte. Oxygen diffuses through the (semi-permeable) membrane to the cathode where it is reduced when an appropriate voltage (.725 V) is applied across the electrodes. The magnitude of the resulting current is proportional to the amount of oxygen present in the sample. Electrode reactions: Anode $4Ag + 4Cl^- \rightarrow 4AgCl + 4e$ Cathode $O_2 + 2H_2O + 4e \rightarrow 4OH^-$
Minimum Detectable Sensitivity	1.0% of full scale
Range	0-5, 0-10, 0-20 ppm by weight of dissolved oxygen
Range Correlation:	±0.25% of full scale for recorder output in going to a less sensitive range
Interferences	Halogens, H_2S, NO(X), SO_2, mercaptans
Multiparameter Capability	Not applicable
Sampling	Method: In situ; continuous flow, 1.5 ft/sec minimum Pressure: 0-50 psig Volume: minimum depth, ; maximum depth, 100 ft Maximum Temperature Input: 55.55°C (132°F) Collection Efficiency: Not applicable Maximum Number of Sample Sources: Limited to <1000 ft from amplifier location (by length of longest specified cable)
Performance	System Accuracy: (a) ±1% of full scale at calibration temperature (recorder output) (b) Sensor accuracy compensated to 6% of reading over full range 0-43.33°C (32-110°F) Reproducibility: ±1% of reading for any temperature, in 24 hrs Linearity: a) Sensor: ±.75% of reading at any given temperature b) Electronics: ±.25% of reading at any given temperature Noise: <±0.5% of F.S. Lag Time: ≤2 sec Rise Time: <20 sec to 90% of final response Retention Time: Not Applicable Fall Time: <20 sec to 90% of final response Zero Drift: <1% in 24 hr at constant temperature Span Drift: <1% in 24 hr at constant temperature Response Time: 90% in 20 seconds or less at constant temperature
Operation	Ambient Temperature Range: -28.89 to 50°C (-20 to 122°F) (Amplifier only) Sample Temperature: 0°-43.33°C (32°-110°F) Temperature Compensation: Two thermistor compensators; one corrects for temperature effect on the sensor itself, the second compensates for the change in solubility of oxygen with temperature Relative Humidity Range: Up to 100% R.H.

Operation (Contd)

Calibration: a) Partial pressure calibration for oxygen in air is achieved by exposing the sensor to air, turning the Range switch to calibrate, and adjusting the Calibrate control so that the meter reads the value for total atmospheric pressure: 760 mm at sea level (7.6 on the scale)
b) Alternately, the instrument may be calibrated by a standard method such as the Winkler. Calibration at least once a month is recommended.
Procedure: Instruction manual supplied with each instrument
Unattended Period: Depends on application - normally 1 to 4 weeks
Maintenance: Depends on process conditions:
Membrane change: every 30 days to 3 months. Membrane need not be removed to replenish electrolyte.
Service period: 3 to 6 months for an average application.

Requirements

Power: a) 115 ±15 volts, 50/60 Hz (cps)
b) 230 ±30 volts, 50/60 Hz (cps)
Weight: Sensor: .227 kg (0.5 lb); Electronic unit: 7.27 kg (16 lbs)
Dimensions: Amplifier: 20.33 cm H x 22.35 cm W x 32.77 cm D (8" x 8-8/10" x 12-9/10" maximum)
Sensor: 8.57 cm diameter x 18.74 cm H (3-3/8" x 7-3/8")

Features

Output: a) Meter readout scales correspond directly to ppm of oxygen: 0-5, 0-10, and 0-20 ppm
b) Potentiometric: 0-10 mV, 0-100 mV or 0-1 V
Training: Sensor may be recharged in the field by non-technical personnel.
Options: Alternate Model, Catalog No. 191601 is available; like 191600, except for additional outputs for current recorders of 0-5, 1-5, 4-20 and 10-50 mA

References

Beckman, Bulletin 4092A, "Dissolved Oxygen Analyzer" and communications, 3/73
For an in-use evaluation see Reference 74 of text.

Cost

Model 735, Catalog No. 191600	$810
Model 735, Catalog No. 191601 (See under options.)	930

Replacement parts:	191605 Sensor	194
	191755 Recharge Kit	39

Accessories:

193661	Cable (1000 ft. maximum, including amphenol connector and loose spade lugs) 20 ft.	$ 38
193662	All other lengths	26 + 0.60/ft.
190705	Submersion assembly	108
190708	In line flow assembly (Pressure compensated)	114
70999	Field mounting kit (for pipe, rail or wall mounting)	27
81778	Instruction manual (1 supplied)	7

Remarks

1) Output signal from solid state amplifier is compatible with virtually all current or potentiometric recorders and controllers, data reduction devices, telemetering systems, and computers.
2) Sensor: The anode, cathode, thermistors and all leads are molded into a PVC body.
3) Note: Each instrument includes: a) Amplifier, b) Sensor P/N 191605, c) Recharge kit P/N 191755, d) Instruction manual P/N 81778. Cable must be ordered separately to length (See Accessories).

Address

Beckman Instruments, Inc.
Process Instruments Div.
2500 Harbor Boulevard
Fullerton, CA 92634
Attn: Lee Braun - Product Line Manager
or
Robert Buchanan - Process Instruments Div. (Ex. 1454)

Dr.Ette Geiger - Sales Analyst (for catalog and price information) (Ex. 1330)
(714) 871-4848

H2O-BIO
Field: DO
Delta 1
Sept. 1975

Dissolved Oxygen Analyzer

Delta Model 2110

DELTA
CALIBRATE
FRESH
SALINITY
BATTERY CHECK
Model 2110 MULTI RANGE ANALYZER For DO, BOD & TEMPERATURE

Class	Laboratory/Field/Portable
Categories of Water	Fresh/Waste
Principle of Operation	The passive type probe has a gold cathode and silver anode connected by a reservoir containing a buffered potassium chloride solution as the electrolyte. A semipermeable (Teflon) membrane confines the electrolyte, and separates it and the electrodes from the solution to be tested. Oxygen from the test solution diffuses through the membrane at a rate proportional to its concentration producing a corresponding flow in the measuring circuit. Temperature effects on oxygen diffusion rates are automatically compensated by the thermistor. Electrode Reactions: Anode $4Ag + 4Cl^- \rightarrow 4AgCl + 4e$ Cathode $O_2 + 2H_2O + 4e \rightarrow 4OH^-$
Minimum Detectable Sensitivity	0.02
Range	0-2, 0-10, 0-20 ppm (mg/l); F.S. adjustable for 0-1, 0-5 ppm
Interferences	Halogens in molecular form, H_2S, mercaptans, NO_x, SO_2
Multiparameter Capability	BOD; temperature

Sampling

Method: Probe in situ
Volume: Min. depth - 1/2 inch
Max. depth - 300 ft
Maximum Temperature Input: 50°C
Collection Efficiency: N/A
Maximum Number of Sample Sources: Unlimited except for 300 ft depth limitation

Performance

Accuracy: Meter - 1% F.S.
Reproducibility: ±1%
Linearity: Linear response
Noise: Negligible
Lag Time: Maximum 30 seconds
Rise Time: Maximum 30 seconds
Retention Time: N/A
Fall Time: Maximum 30 seconds
Zero Drift: Negligible
Span Drift: Negligible

Operation

Ambient Temperature Range: -5° to 50°C; temp. readout provided.
Temperature Compensation: Automatic compensation between -5° and 50°C
Other: Built-in depth and altitude compensation
Relative Humidity Range: Up to 100%
Calibration: Air calibration cable provided
Depth compensation by means of a pressure gland permits submersion up to 300 ft without calibration adjustment.
Procedure: Set mechanical zero, set electrical zero; calibrate unit using a known standard. Using the 0-20 ppm range, immerse probe in sample, agitate sample so that a minimum flow of 1 ft. per second of sample passes over membrane. If reading is lower than 10 ppm, switch to the 10 ppm scale, or lower than 2 ppm, switch to the 0-2 ppm scale.
Unattended Period: May be operated 6 to 9 months without attention
Maintenance: Electrolyte change requires about 2 minutes.
Membrane: Torn membrane may be replaced in about 1 minute.
Other: Replacement kit provides 10 membranes (1 mil) and 2 oz of buffered potassium chloride solution.

Requirements

Power: Rechargeable batteries
Weight: Net weight 9 lbs. (includes battery charger provided with instr.); shipping weight ~ 15 lbs.
Dimensions: 28 cm H x 33 cm W x 20.3 cm D (11" x 13" x 8")

Features

Output: Dual output 0-10 mV; 1) proportional to DO; 2) proportional to temp.
Training: Manual provided with the instrument; see also under Maintenance above.
Options: See under Cost.
Other: Probe is waterproof and submersible to 300 ft. Probe is insensitive to shock, vibration, or changes in temperature and/or pressure within the recommended operating range.

References

Manufacturer's bulletin 2010-AP, May 1971
Additional information provided by Mr. David Anajovitch.

Cost

Model No.	Description	Price
2110-00	Do Analyzer (Price for meter includes battery charge and recorder output connector)	$495
2110-25	Combination DO-temperature probe with 25-ft cable	195
Options:		
2110-100	Probe with 100 ft cable	220
2110-300	Probe with 300 ft cable	290
1010-10	Remote Stirrer on 100 ft cable	190
1010-103	Remote Stirrer on 300 ft cable	215
1010-112	Sample Agitator on 25 ft cable	175

Remarks

Manual salinity compensation; 0 to 40 parts/thousand salinity. A one-year warrantee against defects in materials or workmanship is provided with the 2110 Series analyzer and probes.

User information is available on request.

Output signal may be used to operate proportional control valves or feeders; or for conversion of analog to digital form for input to computer telemetry, and data acquisition systems.

Model 2110 is shipped with a service kit which includes replacement membranes and enough electrolyte for over a year of normal usage.

Address

Delta Scientific Corp.
122 E. Hoffman Ave.
Lindenhurst, NY 11757
Attn: John Becker— Sales Coord. for Laboratory Instr.
or
Robert Mankes—Vice President of Sales
(516) 884-4422

Interferences

SO_2, F_2, Cl_2, Br_2, I_2 and NO_x (<0.25% = 2500 ppm). Mercaptans and H_2S ($\geq$1%) poison sensor.

Multiparameter Capability

Measures oxygen in air between 0-25%

Sampling

Method: In situ probe, 2-3 ft/sec minimum flow
Volume: Minimum depth = 0.25 inches
Maximum Temperature Input: 68.3°C (155°F)
Collection Efficiency: N/A
Maximum Number of Sample Sources: Unlimited

Performance

Accuracy: ±0.2% oxygen in calibration and temperature range
Reproducibility: ±0.1 ppm in water
Linearity: ±1% O_2 from 0-100% O_2, over compensated temperature range
Noise: N/A
Lag Time: N/A
Rise Time: 90% in 10 sec in air; 90% in 10 sec in H_2O
Retention Time: N/A
Fall Time: N/A
Zero Drift: Negligible
Span Drift: <1% O_2 in 2 weeks, when adjusted for atmospheric pressure changes

Operation

Ambient Temperature Range: Sensor: -2.2 to 68.3°C (28 to 255°F)
Analyzer: 0 to 68.3 °C (32 to 155°F)
Temperature Compensation: Sensor compensated between 15-50°C (59-122°F)
Relative Humidity Range: 0-100%, non-condensing
Calibration: Air calibration

Procedure: The sensor is placed in the stream for several minutes to allow equilibration of internal sensor temperature with that of the stream of liquid sample. The sensor is then withdrawn and all water droplets shaken off, leaving the film of moisture on the membrane itself. (This compensates for decreased sensor sensitivity in water.) The instrument is then calibrated in air to 20.9% oxygen and re-inserted into the liquid for reading.

A stirrer may be used to keep renewing the sample at the sensor-liquid interface. In the field this movement may be accomplished in a variety of ways such as siphoning stream water past the sensor. In industrial applications, the sensor is generally installed as an integral part of a pipeline through which the liquid flows. Flow must exceed 2 to 3 ft/second to prevent film formation which results in lower O_2 reading.

Unattended Period: N/A
Maintenance: Sensor must be recharged every 30-60 days

Requirements

Power: 9 V battery (alkali or Hg) included
Weight: .455 kg (1 lb)
Dimensions: 7.6 cm x 12.7 cm x 12.7 cm (3" x 5" x 5")

Features

Output:
Training: Instruction manual provided
Options:

60-601	Replacement Oxygen Sensor with six-foot cable	130.00 ea.
60-602	Disposable Recharge Kits (Box of five)	17.50 box
60-603	6-Foot Sensor Extension Cable	25.00 ea.
60-604	50-Foot Sensor Extension Cable	45.00 ea.
60-605	Carrying Case for Oxygen Analyzer Models #60-600, 60-620, 60-625	5.00 ea.
60-607	Oxygen Nomographs, Pad of 50, 8-1/2 x 11	5.00 ea.

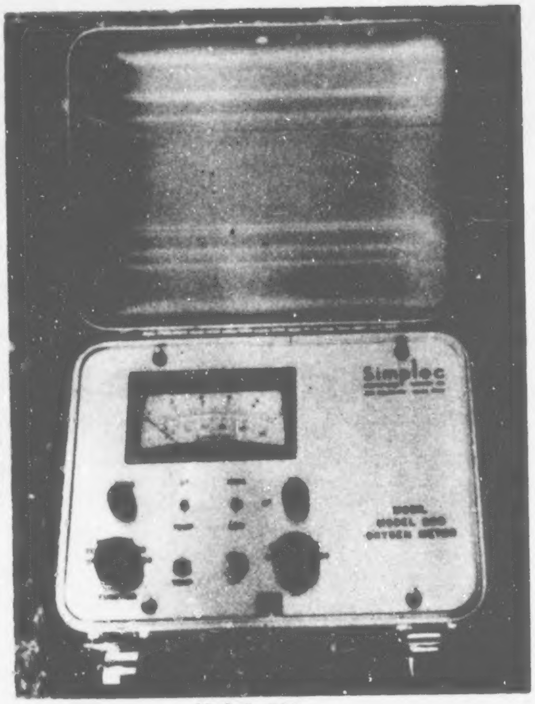
Also available: Model 60-600 - same as 60-620 except with with a 0-50% O_2 scale. Includes O_2 sensor 60-601 and two disposable Recharge Kits. $275. ea.

References	Operating instructions for Edmont Oxygen Analyzers and Monitors, Aug. 15 (1972)	
Cost	Analyzer 60-620 includes sensor, case, and 2 disposable recharge kits	$310.
Remarks	Sensor is fitted with a patented disposable discharge cap which operates at temperatures up to 68.3°C (155°F), and is not damaged by freezing, thawing, mud, oil, or "gummy process chemicals", according to manufacturer's claim. Manufacturer provides a limited 1 year warranty ("provided connector, electrodes and critical surfaces are not worn or damaged in any way.") Warranty does not include batteries. Instruction booklet includes the following conversion tables: a) A nomograph from conversion of Edmont $\%O_2$ to partial pressure in mm Hg or ppm of O_2 by weight. b) A table: Effective Oxygen by Weight Adjusted for Elevation Above Sea-Level (between 0-6000 ft; 50°F only).	
Address	Edmont-Wilson Coshocton, Ohio 43812 (614) 622-4311 Attn: Mike Sweet, Manager of Market Development for Instruments	

H2O-BIO
Field: DO
Fincher 1
Sept. 1975

Dissolved Oxygen
Fincher Oxygen Meter Mobil Model 200

Model 100RT



Model 200

Class	Portable probe
Categories of Water	Fresh/Waste/Salt
Principle of Operation	Amperometric measurement of oxygen by cathodic reduction in a membrane-covered electrolytic cell. An impressed constant voltage reduces all oxygen that diffuses through the membrane to the cathode; the electric current is therefore a measure of the rate of diffusion through the membrane which in turn is proportional to the concentration of oxygen.
	Polarographic cell consists of a gold cathode and silver anode immersed in electrolyte (KCl). The electrodes are isolated from the liquid or gas sample by a fluorocarbon membrane secured by an O-ring. A constant voltage (0.6 V) is impressed on the electrodes. Electrode reactions:
	Anode: $4Ag + 4Cl^- \rightarrow 4AgCl + 4e$
	Cathode: $O_2 + 2H_2O + 4e \rightarrow 4OH^-$
	Overall: $4Ag + 4Cl^- + O_2 + 2H_2O \rightarrow 4OH^-$
Minimum Detectable Sensitivity	5 ppb in solution
Range	.01% to 50% in gases; concentrations in liquids corresponding to equilibrium with gas phase; H_2O, .05 to 25 ppm at 21.1°C (70°F). Range may be expanded to 100% in gases and 50 ppm in H_2O by calibration to a proportional reading.

Interferences

High concentrations of hydrogen sulfide and some gases that can be electrolytically reduced.

Multiparameter Capability

Measures gaseous oxygen and temperature

Sampling

Method: In situ, flowing stream or stirred batch
Volume: 20 cc/min or 400 cc batch
Maximum Temperature Input: 50°C (122°F)
Collection Efficiency: 100%
Maximum Number of Sample Sources: One

Performance

Accuracy: ±.010 ppm in solutions; ±.02% in gases
Reproducibility: 1% of full scale
Linearity: 1%
Noise: Zero without interferences
Lag Time: Less than 10 seconds
*Rise Time: Less than one minute
Retention Time: Zero
*Fall Time: Less than one minute
Zero Drift: 0.1% of full scale per °C
Span Drift: 0.01% of full scale per °C

Operation

Ambient Temperature Range: -5 to +50°C (23-122°F)
Temperature Compensation: Thermistor in probe senses sample temperature which may be displayed by means of the temp-02 switch.
Relative Humidity Range: Zero to saturated
Calibration: Set to 20.8% in air for most applications; for very low concentrations, a reading at zero oxygen is required which is obtained in an auxiliary cell supplied with the instrument.
Procedure: The sensor is calibrated in air and in the zero cell; direct readings are then made in a flowing sample or stirred batch.
Unattended Period: 1000 hours with internal power.
Maintenance: Battery change after 1000 hours operation; occasional membrane and electrolyte change (about 15 minutes required for change).

Requirements

Power: 10 Hg batteries, 1.35 V (Mallory RM12R or equivalent)
Weight: 3.2 kg (7 lbs)
Dimensions: 22.9 x 30.5 x 12.7 cm (9" x 12" x 5"). Lid detachable.

Features

Output: Triple scale meter-- (Gas mixtures) 0-50%; 0-10%; 0-5%; 0-1%; 0-0.5%; 0-0.1%
Training: Manual
Options: Model 100RT (with recorder) $1,275. FOB Houston TX

References

1) Manufacturer's Brochure
2) E.S. Snavely and F.E. Blount, "Rates of Reaction of Dissolved Oxygen with Scavengers in Sweet and Sour Brines," Corrosion 25, 397-404 (1969).
3) E.S. Snavely Jr., "Chemical Removal of Oxygen from Natural Waters," J. Pet. Techn. 23 (4), 443-6 (1971).
4) F.E. Blount and E.S. Snavely, "Use of Oxygen Meter in Corrosion Control," paper no. 44, NACE National Conference, Houston, TX, March 1969. See Proc. 25th Conf. NACE, pp. 193-200, Mar. 10-14, 1970.
5) Manufacturer's Booklet, "Galvanic Probes for the Drilling Industry"

*Electrical rise and fall times are about 0.6 seconds; however, the rise and fall times of the oxygen sensor depend on the magnitude of the change in oxygen concentration; less than one minute is required for 95% of the total rise or fall, but up to 5 minutes may be required for complete equilibrium.

Cost	Model 200	$675. FOB Houston, TX
Remarks	Manufacturer also markets galvanic probes suitable for oxygen monitoring in corrosion control (See Ref. 5).	
Address	Fincher Engineering Co. 6826 Addicks-Fairbanks Rt. 9, Box 909 Houston, TX 77040 Attn: Dorsey R. Fincher, P. E.; Natalie Zolan, Exec. Asst.; J. J. Marr, Engineer; Dr. James W. Ward, Consultant (713) 466-4164	

H20-BIO
Field: DO
Gam Rad Inc. 1
Sept. 1975

Dissolved Oxygen Analyzer

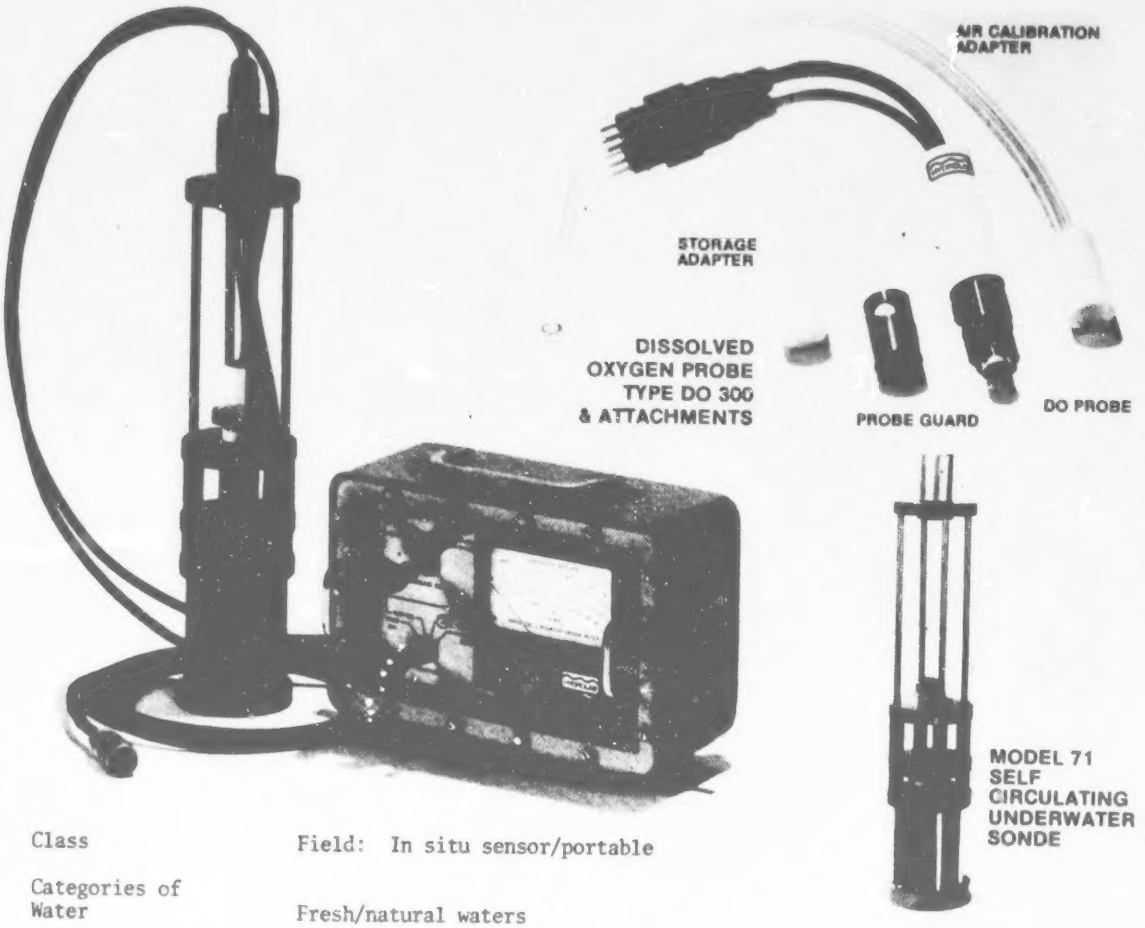
Enviro Monitor Model 1012

Class	Field/Continuous
Categories of Water	Fresh/Waste
Principle of Operation	A passive type polarographic oxygen sensor with a gold cathode and a silver anode, detects oxygen which diffuses across a Teflon membrane and is reduced at the cathode. The magnitude of the current produced is proportional to the partial pressure of oxygen. Electrode reactions: Anode: $2Ag + 2OH^- \rightarrow Ag_2O + H_2O + 2e$ Cathode: $1/2O_2 + H_2O + 2e \rightarrow 2OH^-$ Overall: $1/2O_2 + 2Ag \rightarrow Ag_2O$
Minimum Detectable Sensitivity	.05 ppm (5% of F.S.)
Range	0-5, 0-10, 0-20 mg/l (0-5, 0-10, 0-20 ppm)
Interferences	Strong oxidizing and reducing agents (e.g., HOCl, HF, SO_2, H_2S)
Multiparameter Capability	Up to seven in one monitor
Sampling	Method: In situ or online Volume: Continuous flowing sample Minimum Stream Velocity: 1.5 ft/sec (1/2 gal/min suggested inline flow) Minimum Depth: 8" Maximum Depth: 25' Maximum Temperature Input: 43°C (110°F) Collection Efficiency: N/A Maximum Number of Sample Sources: N/A

Performance	Accuracy: ±1% FS Reproducibility: ±1% of reading at any given temperature/24 hrs Linearity: ±1% of reading at any given temperature/24 hrs Noise: ±0.5% Response Time: 20 sec Lag Time: 12 sec Rise Time: 8 sec Retention Time: Flow dependent; volume = 150 cc in chamber Fall Time: 10 sec Zero Drift: ±1% FS at any given temperature/24 hrs Span Drift: ±1% FS at any given temperature/24 hrs
Operation	Ambient Temperature Range: Electronics: -29°C to 55°C (-20°F to 130°F) Sensor: 0°C to 43°C (32°F to 110°F) Temperature Compensation: Sensor accuracy compensated to 6% of reading over full 32°F to 110°F span Relative Humidity Range: Electronics to 98% Calibration: Air calibrate Procedure: A jet of sample stream is directed against the membrane Unattended Period: 1-8 weeks depending upon application Maintenance:
Requirements	Power: 115 Vac, 60 Hz, 3 A max Weight: 15.9 kg (35 lbs) Dimensions: Electronics: Single channel instrument (Model 512), 25.4 x 25.4 x 17.8 cm (10" x 10" x 7") Multiparameter (Model 1012) Electronics Package, 27.94 cm^3 (11 in^3) Sensor diameter 7.67 cm (3"); length ~12.7 cm (5")
Features	Output: Current: 0-1 ma/1-5 ma/4-20 ma/10-50 ma Potentiometric: 0-10, 0-100 mV; 0-1, 0-5 V Training: Available Options: 1) Plug in alarm module. Adjustable over full range with selected hysteresis. SPDT alarm contacts wired to back terminal board. 2) Maximum cable length 2000 ft. Others: Sensor housings have PVC and stainless steel construction throughout
References	Enviromonitor Bulletin 1012 Information provided by the manufacturer (telephone conversations with Mr. Trawick, 6/5/74 and 6/11/74)
Cost	Includes housing, transmitter, sensor, E to I converter and 25 ft of cable $1050.
Remarks	Assembly can be mounted in-line in a flow-through housing with entrance and exit ports on opposite sides. The sensor is supplied by a pipe connected to the top of the housing. The monitor is threaded through the pipe to the sensor. The DO monitoring assembly is supplied with a standard 25' cable. Other cable lengths available on request.
Address	Gam Rad Inc. 16825 Wyoming Avenue Detroit, Mich. 48221 Attn: William Helke, General Manager for Sales of Industrial Products; Dan Mapes, Applications Engineer (313) 864-6006

H2O-BIO
Field: DO
Hydrolab 1
Sept. 1975

Dissolved Oxygen Temperature Meter
Hydrolab Model TDO-2


AIR CALIBRATION ADAPTER
STORAGE ADAPTER
DISSOLVED OXYGEN PROBE TYPE DO 300 & ATTACHMENTS
PROBE GUARD
DO PROBE
MODEL 71 SELF CIRCULATING UNDERWATER SONDE

Class	Field: In situ sensor/portable
Categories of Water	Fresh/natural waters
Principle of Operation	A passive gold-silver/polarographic cell is fitted with a gas-permeable (1 mil Teflon) membrane through which oxygen from the surrounding medium may diffuse into the probe and be reduced at the cathode. The current required by the probe for reduction of the diffusing oxygen is linearly proportional to the partial pressure of the oxygen present in the medium. Electrode reactions: Anode $4Ag + 4Cl^- \rightarrow 4AgCl + 4e$ Cathode $O_2 + 2H_2O + 4e \rightarrow 4OH$
Minimum Detectable Sensitivity	.05 ppm
Range	0-10 (100 Divisions), 0-20 ppm (or mg/l), 0-100% saturation
Interferences	SO_2, H_2S, halogens poison the silver electrode.
Multiparameter Capability	Temperature not recorded separately.
Sampling	Method: Automatic sample-circulating sonde Volume: Minimum depth - sensor: 1/2 inch/not recommended sonde: 8-10 inches Maximum depth: 100 meters (330 ft) Maximum Temperature Input: 45°C Collection Efficiency: N/A Maximum Number of Sample Sources: Limited by maximum cable length to 100 meters/setting; otherwise unlimited

Performance

Calibrated DO Accuracy: Output data signal: ±2% of reading
Meter: ±2% of reading to 0.5% of range
Temperature: ±0.5°C
Reproducibility.
Linearity: Meter: 0.5%
Noise:
Response Time: 10 sec to stepchange in DO
30 sec to stepchange in temperature
Lag Time:
Rise Time:
Retention Time:
Fall Time:
Zero Drift:
Span Drift:
Readability: 0.1 ppm for 0-10 ppm setting of water

Operation

Ambient Temperature Range: -5° to 45°C
Temperature Compensation: Membrane dependence and oxygen solubility temperature coefficient are automatically compensated.
Relative Humidity Range: Up to 100% relative humidity
Calibration: Dissolved oxygen: Air, or Winkler standardized oxygen solution
Temperature: May be verified against an internal standard
Procedure: In operation, the sonde and probe are lowered at the end of an underwater cable to a desired measuring depth and the DO concentration and temperature of the water at that depth are read directly from the instrument meter. The output may be recorded as DO or partial pressure as a function of time.
Unattended Period: Minimum one week and up to six weeks
Maintenance: Depends on use. In fresh water the analyzer may run 24 hours/day for approximately 2 weeks prior to preventive maintenance. Time required to load and purge probes -- about 30 seconds.

Requirements

Power: Instrument: Three TR-132R or E-132N mercury batteries
Voltage: 2.7 V; stirrer - 9 V lantern battery
Battery Life: About 500-600 instrument hours
Sample Circulation: 130 mA, 6 or 9 Vac (lantern type battery), depending on cable length
Weight: Surface Unit: 2.7 kg (6 lbs)
Sonde: 1 kg (2.2 lbs)
Cable: 1.5 kg (3.3 lbs)
Probe: ca. 6 oz
Dimensions: Inst. Encl.: 30 x 19 x 16-1/2 cm (12 x 7-1/2 x 6-1/2 in.)
Sonde: 39 cm (15-1/2 in.)
Cables: Standard lengths: 10, 20, 50, 100 m
(See also Summary for optionals)

Features

Output: Data signal: 0-10 millivolts
Output resistance: 500 ohms
Training: Manual provided.
Membrane change may be done by non-technical personnel.
Options: For continuous recording the TDO-2 may be used in conjunction with a Hydrolab Model 400-M recorder which records DO vs time for periods up to 7 days.
Other: Controls, electronics, batteries and readout meter are protected from outside air and moisture by means of the TDO-2 case which is fitted with gasket or o-ring seals at all openings.

Instrument unit may be floated in water.

Controls extend via shaft seals through a heavy plastic viewing window for total water sealing during instrument operation.

References

Hydrolab Model TDO-2 Brochure and information provided by Mr. Jim Flynn of Hydrolab Corporation.

Cost

Basic package includes the instrument, one cable, and a maintenance kit (electrolyte, 30 membranes, and o-rings)

Model TDO-2, surface unit	$570
Probe	270

Remarks

The Model TDO-2 is used in conjunction with a type 10 CS underwater cable, a DO-3 oxygen-temperature probe and a type 71 sonde for making in situ measurements of DO.

Cables are type 10C multiconductor, urethane jacketed with oceanographic subsurface connectors and environmental surface connector; breaking strength, 300 lbs.

Measurements at different depths permit construction of DO-temperature profiles.

Electrolyte: Half-saturated KCl solution

Summary

Part (type)	Weight		Dimensions	Cost
Standard cables: (urethane)	kg	(lb)		
10C-10	1.135	2.5	10 m (33 ft)	$250
10C-20	2.043	4.5	20 m (66 ft)	270
10C-50	4.767	10.5	50 m (165 ft)	340
10C-100	9.307	20.5	100 m (330 ft)	450
Field case (sealed, waterproof)	2.7 kg (6 lb)		30 x 10 x 16.5 cm (12 x 7.5 x 6.5 in)	110
Sonde model	1 kg (2.5 lb)		39 cm L x 8.5 cm diam. (15-1/2 x 3-1/4 in.)	260

Address

Hydrolab Corporation
P. O. Box 9406
Austin, Tx 78766
Attn: Mr. Jim Flynn or Ms. Tess Peterson
(512) 837-2050

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

H20:BIO
Field:DO
IBC 1
June 1975

Dissolved Oxygen and Temperature Monitor

IBC Model 490-051

IBC
INPUT
CALIBRATE
CHECK

Class	Field/Laboratory/Portable
Categories of Water	Fresh/Saline/waste

Principle of Operation

The oxygen sensor consists of a polarographic cell which measures partial pressure of O_2 in a gas or liquid. The anode, cathode and electrolyte gel of the sensor are separated from the sample by a semi-permeable teflon membrane (1 mil) across which the oxygen may diffuse. A polarization voltage (V) is applied across the electrodes. In the absence of oxygen, no current flows, but when O_2 is present in the sample, it will diffuse across the membrane at a rate proportional to its partial pressure (P_{O_2}) in the solution and be reduced at the cathode. Current flow is a linear function of the P_{O_2}. Overall reaction:

$$O_2 + 2H_2O + 4e \rightarrow 4OH^-.$$

Thus for every molecule of O_2 reduced at the cathode, 4 electrons are given up by the cathode and 4 hydroxyl anions (OH^-) are formed and migrate to the anode.

For O_2 measurement, the instrument operates as a current amplifier for current generated in the sensor. The amplified current drives the indicator meter. Polarizing potential is supplied by a separate circuit.

Since polarographic sensors have temperature coefficients, current output increasing with temperature for a given P_{O_2}, and the O_2 solubility shows appreciable temperature-dependence, automatic temperature compensation which controls amplifier gain is built into the sensor by means of a temperature sensing thermistor.

Minimum Detectable Sensitivity	
Range	0-5, 0-15 ppm.
Interferences	Free Halogens, H_2S, NO_x
Multiparameter Capability	Temperature, BOD
Sampling	Method: In situ sensor Volume: N/A Minimum Depth: 0-12 inches, depending on sensor. Maximum Depth: 500 ft. Maximum Temperature Input: 50°C Collection Efficiency: N/A Maximum Number of Sample Sources: N/A
Performance	Accuracy: ±0.1, 0-5 ppm; ±0.2,10-15 ppm, ±1°C Reproducibility: Better than 0.1 ppm Linearity: D.O.: ±1% F.S.; Temperature: ±1°C max. error Noise: Lag Time: 1 sec Retention Time: N/A Fall Time: See response time Response Time: 90% in 30 sec. Zero Drift: +0.1 ppm max. Span Drift: Negligible between calibrations
Operation	Ambient Temperature Range: 0-50°C Temperature Compensation: ±0.1 ppm max. error when calibrated within ±5°C of sample temperature Relative Humidity Range: 0-100%

Calibration: Since individual sensor cartridges vary, each must be calibrated. In addition, long term sensor drift requires periodic calibration. Calibration should be repeated every 24 hours, even under constant operating conditions.

For the greatest accuracy, polarizing voltage should be applied to the sensor for a minimum of 15 minutes before calibration. Simple and accurate calibration may be accomplished by exposing the sensor to ambient air. Correction tables are supplied in the operating manual for total pressure, salinity altitude, and humidity. The corrected reading will be equal to that of water saturated with air under identical conditions.

Calibration may also be accomplished by measurement of a water sample that has been prepared in a tonometer with a known gas, or a Winkler titration for dissolved oxygen may be used for calibration.

Procedure: The appropriate sensor is connected to the assembly through the front panel INPUT connector. The "CALIBRATE" knob on the face of the instrument is tuned to bring the meter reading into agreement with the calibration medium. Although recalibration every 24 hours is suggested, long term in situ monitoring may be accomplished with any required corrections applied at the end of the monitoring period.

The temperature reading requires no calibrations or preliminary warmup.

Once calibrated, the sensor may be placed in the water to be analyzed. Two scales are available, 0-5 and 0-15 ppm dissolved oxygen and the applicable scale should be selected.

Fast equilibration time permits rapid readings even under highly variable conditions. Stirring is provided on Deep Diver and BOD Sensors and is optional on the Shallow Diver.

A rotary switch has the following operating positions:

(1) OFF: all power is disconnected;
(2) CHECK: monitors battery voltage:
(3) TEMP: Indicates temperature on the red scale (0-50° C)
(4) 0-15: Dissolved Oxygen (D.O., 0-15 ppm) on the black scale
(5) 0-5: Dissolved Oxygen (0-5 ppm) on the green scale

The CALIBRATE control is active only in the D.O. measuring positions and adjusts the gain (span) of the instrument to calibrate the sensor. (See under calibration)

Unattended Period:

Maintenance:

Requirements:

Power: 4 "C" size batteries (Eveready E93 or equivalent) and one mercury cell (Mallory RM502R or equivalent)
Weight: 2 Kg(4.4 lb)
Dimensions: 17.8 x 15.2 x 11.4 cm(7"x6"x4½") (HxWxD)

Features:

Output: To meter read out. See under options.

Training: Instruction Booklets
Options: May be used with D.O. Sensor(with stirrer) Cat. no. 501-001 Deep Diver and/or with BOD sensors 410-001 and 410-011. The monitor may also be used with DO Sensor 600-01, Shallow Diver (10 ft lead standard)

Lead lengths are available in multiples of 25 feet up to 50 ft.

A splashproof recorder output is available on special order, 0-1 V.

References:

IBC Instruction Booklet: "IBC Dissolved Oxygen & Temperature Monitor Field Unit" (Cat No. 490-051)
IBC Dissolved Oxygen Sensor With Stirrer (Cat. No. 501-001)

Cost:

490-051	Field Model (price without electrodes) batteries included	$450.00
500-051	BOD, DO and Temperature Analyzer	380.00
Options:	Laboratory Model	
300-061	Compact Model	230.00

Instruments and Sensors with Waterproof Connectors for use with Models 490-051, 500-051, and 300-061 Analyzers

410-001	BOD Sensor, 5 ft lead	$170.00
412-001	Replacement Cartridge, BOD	25.00
600-001	Shallow Diver, DO, 10 ft lead	120.00
600-021	Shallow Diver, DO, 50 ft lead	135.00
620-001	Stirring Unit, Deep and Shallow Diver	125.00
501-001	Deep Diver, DO, with Stirrer, 25 ft	280.00
501-011	Deep Diver, DO, with Stirrer, 50 ft	290.00
501-021	Deep Diver, DO, with Stirrer, 75 ft	300.00

Other lengths up to 500 ft available in multiples of 25 ft. Please specify length desired and add $10.00 for each 25 ft ordered.

526-001	Replacement Cartridge, DO	25.00

Remarks:

This instrument uses battery-powered integrated circuitry, and is packaged in a "splash-proof" case. It is specifically designed for "reliable operation under adverse conditions".

The instrument as originally shipped is equipped with long-life alkaline power batteries(Eveready E93 or equivalent) and a mercury reference battery (Mallory RM502R or equivalent). Reference batteries should be 1.30-1.35V at room temperature.

The following sensors are recommended for use with this assembly:

1) IBC DO sensor with stirrer, Cat. No. 501-001.
2) IBC Biological oxygen Demand Sensor, Cat. No. 410-001.

Both sensors are designed to use replaceable sensor cartridges.

Readings from the Model 501-001 Deep Diver and 600-001 Shallow Diver are both pressure and temperature compensated.

In-line measurements of temperature and D.O. are available with special sensor modifications.

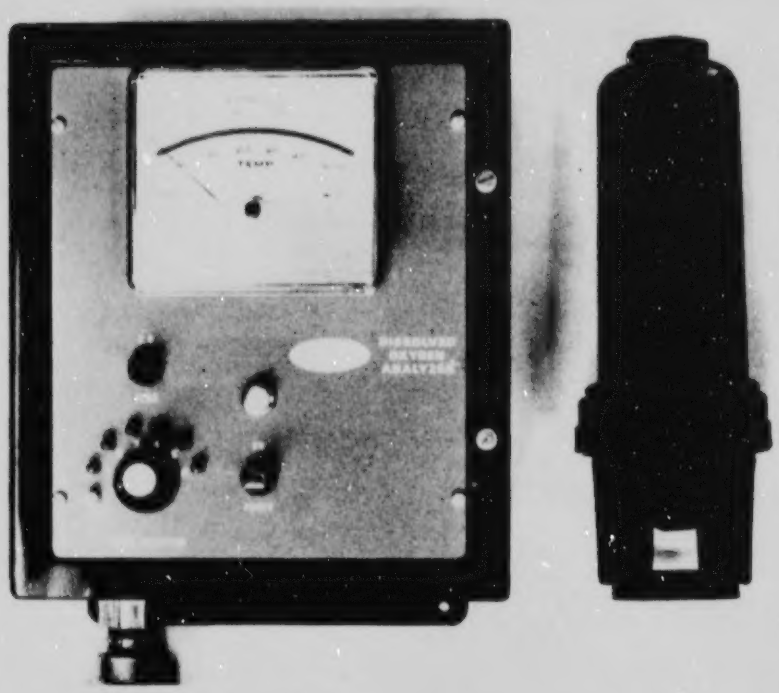
Instruments and sensors (except cartridges) warranted against defects in materials (essentially PVC) and workmanship for one year. Cartridge life is in the range of 4-6 months and is dependent on care outlined in the operating manual.
Both sensors are designed to use replaceable sensor cartridges.

Address:
International Biophysics Corporation
2700 DuPont Drive
Irvine, CA 92664
Attn: Robert E. KLees
Vice President of Marketing

Gilbert M. Bockhaus, Sales Manager
(714)833-3300

Dissolved Oxygen Analyzer

Ionics Model 1131S



Class	Continuous online
Categories of Water	Waste (Designed primarily for the measurement and control of Dissolved Oxygen concentration [DO] in activated sludge aeration basins)
Principle of Operation	The corrosion potential generated between an exposed Tl metal electrode and a reference electrode is proportional to [DO]. Electrode reactions: Anode: $4Ag \rightarrow 4Ag^+ + 4e$ Cathode: $O_2 + 2H_2O + 4e \rightarrow 4OH^-$ Overall: $4Ag + O_2 + 2H_2O \rightarrow 4AgOH$
Minimum Detectable Sensitivity	0.1 ppm
Range	0.5-5 ppm, 1-10 ppm, 1.5-15 ppm; optional ranges up to 15 ppm DO and 50°C available on special order
Interferences	Large conductivity changes
Multiparameter Capability	Temperature
Sampling	Method: In situ, continuous flow; 5 ft/minute, minimum Volume: Depth up to 25 ft. For greater depths, consult manufacturer Minimum Depth: 1 ft Maximum Temperature Input: 50°C Collection Efficiency: N/A Maximum Number of Sample Sources: 6 Maximum Distance to Analyzer: 1000 ft. Sample Flow Rate: minimum 5 ft/min.

Performance

Accuracy: DO: ±0.3 ppm or ±3.0% of reading, whichever is larger (at constant temperature)
Temperature: ±1°C
Reproducibility: ±2%
Linearity: Direct linear readout of ppm DO and temperature in °C
Noise: N/A
Lag Time: N/A
Rise Time: DO: 15 second max. for 95% F.S. @ constant temperature. A sensor damping filter increases response time to 1 minute maximum.
Temperature: 3 min max. for 95% step change
Retention Time: N/A
Fall Time: N/A
Zero Drift: DO: 0.1 ppm/30 day period
Temperature: 0.3°C/30 day period
Span Drift: <1%/month

Operation

Ambient Temperature Range: 0-50°C
Temperature Compensation: Compensated between 10-50°C
Relative Humidity Range: 0-85%
Calibration: Winkler titration

The following procedure is recommended when starting up a new analyzer, or adjusting the analyzer to changing conditions.

A. Temperature Calibration
   1. Measure the temperature of the water at the probe with an accurate thermometer.
   2. Switch temperature - DO switch located on the front of the control cabinet to TEMP.
   3. For a multiprobe unit, select the proper probe with the probe selector switch (front panel).
   4. Remove the plexiglas cover plate located inside the analyzer and adjust the temperature - adjust control for the probe to be calibrated. This procedure is repeated for all probes. For a multiprobe instrument the temperature test reading will be the same for all probes.

B. Dissolved Oxygen
   1. Place the probe in the flowing stream.
   2. For multiprobe analyzers place the probe selector switch in the position corresponding to the correct probe.
   3. Switch the temperature-D.O. switch to D.O.
   4. Switch AC power on and allow for warm-up (i.e., the indicating meter shows no drift).
   5. Collect one gallon of water in a bucket from the stream and bubble air into the sample to maximum D.O. (saturation).
   6. Position the probe in the bucket.
   7. Determine the actual D.O. content of the sample by an appropriate modification of the Winkler procedure.
   8. Adjust the input zero control so that the meter will indicate the D.O. value.
   9. Repeat the Winkler calibration until values differ by < .25 ppm and the D.O. value in the sample is steady, readjusting input zero control to get correct meter readings each time.
   10. This completes the calibration and the probe may be returned to the flowing stream for measurements.

Unattended Period: 1-5 weeks depending on sample
Maintenance: Once every 6 weeks;trim electrodes

Requirements

Power: 0.1 A @ 115 V ±10 Vac, 50/60 Hz (220 V available on request)
Weight: approx. 4.5 Kg (10 lbs.)
Dimensions: 27.3 cm H x 23.5 cm W x 14.6 cm D (10-3/4" x 8-1/4" x 5-3/4")
Maximum Distance of Sensor from Analyzer: 1000 ft
Environmental Conditions: Analyzer: Should be sheltered from direct exposure to weather
Sample: Output may be affected by changes in conductivity and/or flow rate. Materials in contact with sample: Ti metal, epoxy, polypropylene, glass ceramic, stainless steel and neoprene

Features

Output: 0-50 mV potentiometric or 0-50 μA; 1000 ΩDC recorders
Standard Outputs:

Meter: DO: 5 ppm F.S., 10 ppm F.S., 15 ppm F.S.
Temperature: 0-50°C

Options: Probe is also available in a flow chamber configuration which may be inserted into a pipeline by means of 3/4-inch pipe connections.

1131 AS Electronics for multiple switching unit. $1250.00
Permits automatic or manual switching of the single inputs of up to six probes. May be used with multipoint recorder model 1131 MPR. Probes separate.

1131 025 Probe assembly. $300.00
Includes thallium and reference electrodes in a polypropylene housing designed for standard submersible use. Cable separate.

Output Options: Any F.S. voltage up to 5 volts
Meter: Other scales available limited to 15 ppm maximum.
Current Output: 1-5, 4-20, or 10-50 mA current outputs are also available.
Optional Accessories:

1) 1131 MPR - 6 point multipoint recorder $1525.00
2) 11310 2F - In-Line Probe Assembly. The sensors are available in in-line flow configuration having 3/4" NPT inlet and outlet fittings. 325.00
3) DO/Temperature Switching Unit: Allows DO and temperature to be recorded from the same analyzer using either a single- or multipoint pen recorder. 395.00
4) Mounting Brackets: A number of suggested arrangements are available:
   1131 P - panel mounting kit for mounting electronics 25.00
   1131 BRK - mounting bracket for waste treatment plant aeration basin 65.00
5) 1131 NIV - Dust Proof water-tight enclosure for electronics. 175.00

References

1) Ionics Bulletin "Dissolved Oxygen Analyzer Model 1131"
2) Ionics Instruction Manual, Series 1131, Dissolved Oxygen Analyzers
3) Manufacturer's letter of May 10, 1974

Cost

Model 1131S (Single probe unit) $695.00

Remarks

Self-cleaning sensor consists of metallic thallium electrode, reference electrode, and temperature sensitive resistor.

The electrodes, and a temperature sensor, are mounted in a plastic probe fitted on top with a terminal strip for cable connections. The connector is protected by a gasketed watertight probe housing threaded on top to receive 1-inch conduit or pipe which supports the probe in the water and provides access for the shielded cable connecting sensors with the analyzer cabinet.

Automatic or manual switching units can handle signals from up to six separate probes.

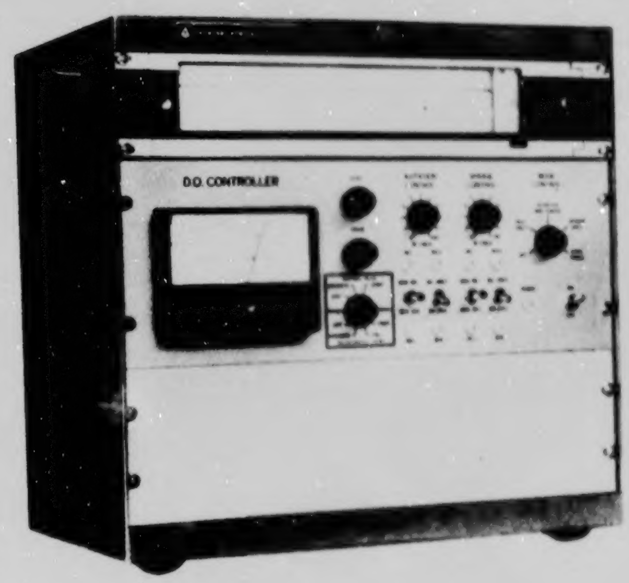
Address

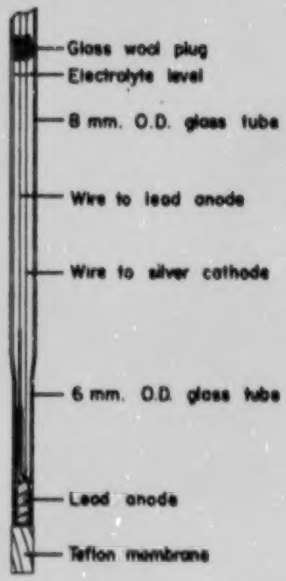
Ionics
65 Grove St.
Watertown, MA 02172
Attn: Floyd H. Meller, Technical Director, Instrument Division, or
Steven A. Michalek, Instrument Division, Applications Manager
Elizabeth Greene, Sales
(617) 926-2500

H2O-BIO
Field: DO
NBS 1
Sept. 1975

Dissolved Oxygen Controller

New Brunswick Scientific Model DO 81


D.O. CONTROLLER

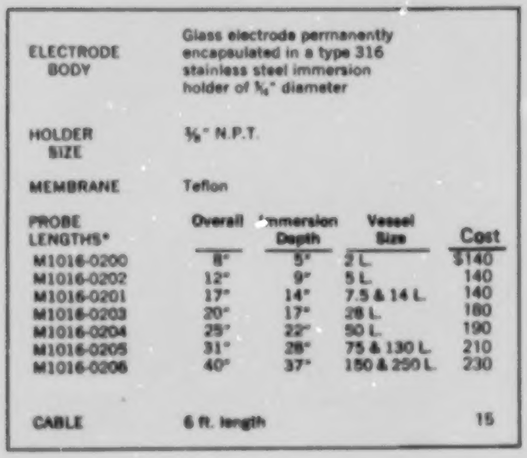

Glass wool plug
Electrolyte level
8 mm. O.D. glass tube
Wire to lead anode
Wire to silver cathode
6 mm. O.D. glass tube
Lead anode
Teflon membrane

Probe

Class	Batch/Continuous (Laboratory/Industrial)
Categories of Water	Fresh/Waste
Principle of Operation	A galvanic type electrode uses a silver cathode and lead anode with acetate buffered electrolyte (5 M HAc + 0.5 M NaAc + 0.1 M $Pb(Ac)_2$) confined by a Teflon membrane permeable to O_2. Inside the membrane the O_2 content is kept very low by the electrochemical reaction. Thus the rate-determining step for oxygen reduction is in effect the rate of oxygen diffusion across the membrane. The latter rate depends on the partial pressure of oxygen (oxygen tension) in the solution in contact with the membrane. Electrode reactions: Anode $Pb \rightarrow Pb^{++} + 2e$ Cathode $\underline{1/2O_2 + H_2O + 2e \rightarrow 2\,OH^-}$ Overall $Pb + 1/2O_2 + H_2O \rightarrow Pb(OH)_2 \xrightarrow{[2CH_3COOH]} Pb(Ac)_2 + 2H_2O$
Minimum Detectable Sensitivity	0.00002 Atm. O_2
Range	0-100% O_2 saturation
Interferences	sulfide conc. should be less than 40,000 Mg./ml.
Multiparameter Capability	N/A.
Sampling	Method: Batch/Continuous Volume: Varies with length of probe Maximum Temperature Input: 60°C Collection Efficiency: N/A Maximum Number of Sample Sources: One

Performance	Accuracy: ±2.0% of O_2 saturation Reproducibility: ± 1% O_2 saturation Linearity: Response linear from <0.00002 to >0.2 atm O_2 Noise: Not detectable Lag Time: Instantaneous Rise Time: 90% response in 45 seconds; probe, 99% response in ~3 minutes Retention Time: Instantaneous Fall Time: 90% response in 45 seconds; 99% response in ~ 3 minutes. Zero Drift: 0.2 MV. Span Drift: Not more than 1%/week Zero Current: <0.1% of O_2 saturation
Operation	Ambient Temperature Range: 20-60°C Temperature Compensation: None Working Pressure: Up to 50 psig Relative Humidity Range: 0-100% O_2 saturation Calibration: Probe is calibrated in air (after wetting so that membrane has a film of H_2O) and in air-saturated water. Procedure: The micro-sized probe is readily mounted in a small vessel, either by insertion into a rubber stopper or compression fitting. It may be mounted vertically or sloped. Larger probes are sheathed in stainless steel housings. A variety of adaptors and probe mountings are available. Unattended Period: 1 year with repeated autoclaving Maintenance: Maintenance-free for long periods
Requirements	Power: Analyzers and controllers - 115 V, 60 Hz or 220 V, 50 Hz 1 phase, AC Weight: ~ .23 - 1.4 Kg (~ 1/2 lb - 3 lb.) Dimensions: Probe: 8 lengths available (see table under Options) Cable: 6 ft Controller:
Features	Output: 10 mV, 1000 Ω 10 μA @ 30°C and 100% O_2 saturation Zero current <0.1% of O_2 Training: Operating Manual Options: Probe lengths from 8" to 53"

PROBE SPECIFICATIONS



ELECTRODE BODY	Glass electrode permanently encapsulated in a type 316 stainless steel immersion holder of ¼" diameter			
HOLDER SIZE	⅜" N.P.T.			
MEMBRANE	Teflon			
PROBE LENGTHS*	Overall	Immersion Depth	Vessel Size	Cost
M1016-0200	8"	5"	2 L.	$140
M1016-0202	12"	9"	5 L.	140
M1016-0201	17"	14"	7.5 & 14 L.	140
M1016-0203	20"	17"	28 L.	180
M1016-0204	25"	22"	50 L.	190
M1016-0205	31"	28"	75 & 130 L.	210
M1016-0206	40"	37"	150 & 250 L.	230
CABLE	6 ft. length			15

Features (cont'd.)   Options:

O_2 ELECTRODE (Less Cable and Adapters)

PART NO.	DESCRIPTION				FOB PRICE
	COMPONENTS	OVER-ALL LENGTH†	IMMER-SION DEPTH	FERMENTOR SIZE	
M1016-0202	O_2 Electrode Steam-Sterilizable with Immersion Holder and Shorting Jack	12"	9"	5 Liters	$140
M1016-0201		17"	14"	7.5 & 14 Liters	$140
M1016-0203		20"	17"	20 Liters	$180
M1016-0208	Dissolved O_2 Glass Electrode, repeatedly autoclavable, (less connecting cable) 17.5 cm immersion depth				$115

CONNECTING CABLE

P0720-2010	6 ft. length* with amphenol plug for connection to electrode, and pin-jack terminals.	$15

*Additional lengths available at 50¢ per ft. additional.

O_2 ANALYZERS & CONTROLLERS (LESS ELECTRODE)

Please Specify Size of Culture Vessel and Electrical Service

MODEL NO.		DESCRIPTION	ELECTRICAL SERVICE	FOB PRICE
1	DO-40	O_2 Indicator		$525
2	DO-50	O_2 Indicator and Recorder		$825
3	DO-81	O_2 Indicator, Expanded View Recorder and Exponential Controller for bench scale equipment	115 V 60 Hz and 220 V 50 Hz, 1 Phase, A.C.	$3,340
3	DO-82	Same as above but panel-mounted in pilot plant fermentors		$3,340
P0540-1010		Chart Paper, O_2 recorder, (31-day) calibrated in % O_2, 6 rolls/ctn. 1 carton supplied with DO-50 and DO-80 series.		$40/ carton of 6

References

a) Manufacturer's Brochure "Dissolved Oxygen Electrodes and Control Systems"

b) M.J. Johnson, J. Borkowski, and C. Engblom, "Steam Sterilizable Probes for Dissolved Oxygen Measurement", Biotechnology and Bioengineering VI, pp. 457-68 (1964); *ibid.* IX (4), "Communications", pp. 2-6 (1967) (NBS reprint booklet).

Cost

Model DO 81 (less electrode)	$3340

Remarks

Probe life expectancy manufacturer claims in excess of 1 year of continuous use with repeated sterilization. Can be used with three different instruments for O_2 measurement and control.

The model DO-81 dissolved Oxygen Controller was designed primarily for use with NBS fermentation equipment. For other applications the Model DO-40 Dissolved Oxygen Indicator or the Model DO-50 Indicator/recorder are recommended by the manufacturer. (See table 1, p. 3.)

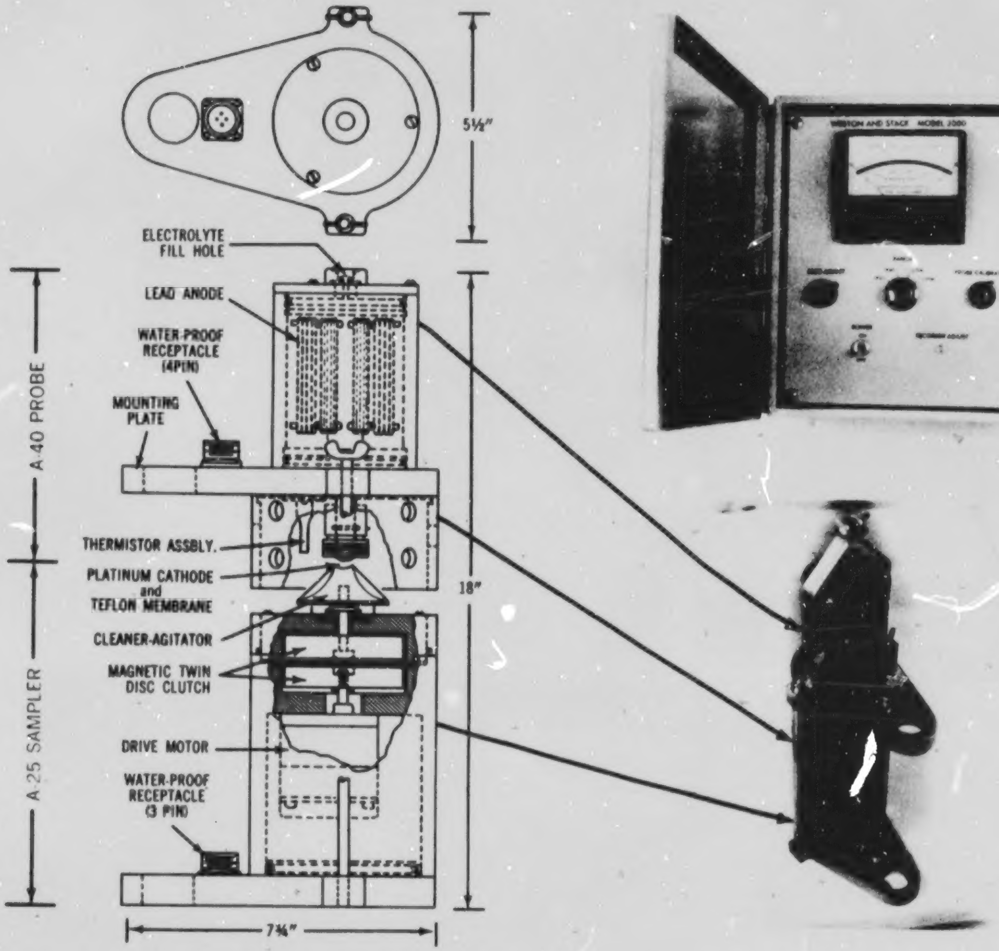
Address

New Brunswick Scientific Co., Inc.
1130 Somerset Street
New Brunswick, NJ 08930
Attn: Ezra Weisman, Sales Manager
Tel: (201) 846-4600

H2O-BIO
Field: DO
Weston and Stack 1
Sept. 1975

Dissolved Oxygen Analyser

Weston and Stack Model 3000


5½"
ELECTROLYTE FILL HOLE
LEAD ANODE
WATER-PROOF RECEPTACLE (4PIN)
MOUNTING PLATE
A-40 PROBE
THERMISTOR ASSBLY.
PLATINUM CATHODE and TEFLON MEMBRANE
CLEANER-AGITATOR
MAGNETIC TWIN DISC CLUTCH
A-25 SAMPLER
DRIVE MOTOR
WATER-PROOF RECEPTACLE (3 PIN)
18"
7¾"
WESTON AND STACK MODEL 3000

Class	Continuous-sensor, stationary
Categories of Water	Fresh/Saline/Waste (sewage - activated sludge)
Principle of Operation	A polarographic cell consisting of a lead anode and platinum cathode functions galvanically, producing 0.6 volts potential. The probe is separated from the sample by a semipermeable membrane. For a given set of physical conditions the rate of diffusion across the membrane is directly related to the concentration of oxygen in the sample. Electrode Reactions: Anode: $Pb + 2OH^- \rightarrow PbO + H_2O + 2e$ Cathode: $1/2\ O_2 + H_2O + 2e \rightarrow 2OH^-$ Overall: $Pb + 1/2\ O_2 \rightarrow PbO$
Minimum Detectable Sensitivity	.05 ppm on 0-15 ppm scale .005 ppm on 0-1.5 ppm scale
Range	0-1.5, 0-15 mg/l (ppm); 0-50°C ±1°C
Interferences	Limited to gases to which the membrane is permeable, and which can be reduced by hydrogen at -0.578 V (e.g., free chlorine gas and NO_x). Not affected by H_2S

H20-BIO
Field: DO
Weston and Stack 1
Sept. 1975

Multiparameter Capability

Direct temperature readout, 0°-50°C

Sampling

Method: Continuous
Volume:
Maximum Temperature Input: 50°C
Collection Efficiency:
Maximum Number of Sample Sources: Probe may be placed at any desired point in the system.
Minimum Flow Rate: None. Pumping and agitation is built in.

Performance

Accuracy: 1% of reading on either DO scale; limited by meter movement
Reproducibility: Better than 0.1 ppm on the 0-15 ppm scale; 0.5% with recorders
Linearity:
Noise:
Lag Time:
Response Time: Function of membrane thickness

Up scale	Down scale
1/2 mil - 15 sec	1/2 mil - 20 sec
1 mil - 30 sec	1 mil - 90 sec
2 mils - 1 min	2 mils - 180 sec

Retention Time:
Fall Time:
Warm-up Time: Approximately 15 min
Zero Drift: <.05 ppm long term drift
Span Drift: <.01 ppm/°C drift
Depth: 350 ft (maximum tested); minimum - about 4 inches

Operation

Ambient Temperature Range: 0-50°C ±1°C
Temperature Compensation: Thermistor compensates within ±2% over the temperature range (0-50°C); ±1% within 10°C span of probe.
Relative Humidity Range: Up to 100%

Calibration: a) Recommended procedure: Remove probe from aeration basin, rinse to remove accumulated solids, and place it in a bucket of tapwater. The DO concentration is determined first by the Winkler titration. Sample water should be slightly warmer than ambient temperature and nearly saturated with oxygen so that the DO level does not change significantly during calibration.

b) Alternate procedure: Remove probe from aeration basin and expose it to air for about 15 minutes. As the probe dries, the assembly approaches ambient temperature and the output is equivalent to that of water saturated with oxygen at ambient temperature. The ambient temperature is obtained by switching the selector knob to the temperature position and the appropriate DO value may then be read from a table of saturation DO values for pure water. Note: This method is not suitable for waste water containing >1,500 mg/1 dissolved solids.

Procedure: The assembly, including the A-40 DO probe and the A-25 cleaner-agitator, is submerged in the activated sludge mixed liquor. Cables with waterproof connectors bring power to the motor in the cleaner-agitator unit and transmit signals from the probe and thermistor to the DO analyzer.

Unattended Period:
Maintenance: Varies with use: Based on an uninterrupted (unruptured) membrane under normal conditions the analyzer may run as long as 6 months, but preventive maintenance is recommended every 30 days.

Requirements

Power: Sampler: 110 Vac or battery operated with high efficiency inverter 10 watts power drain by motor at 280 rpm
Weight: Analyzer-- 10 kg (22 lb). A40 Probe/A25 Agitator -- 6.4 kg (14 lb)

Requirements (Cont'd)

Dimensions: Model 3000-1-A--Wall Mount JIC Type--30.5 cm x 20.7 cm 14 cm (12" x 10-1/2" x 5-1/2")
Model 3000-1-B--Rack Mount Panel--48.3 cm x 22.2 cm x 33 cm (19" x 8-3/4" x 13")
Model 3000-1-C--Panel Mount, Slideout Chassis-- 15.25 cm x 15.25 cm x 43.2 cm (6" x 6" x 17")

Features

Output: Recorder: 0-1 V full scale output for both ranges
Current output recorder: 0-10, 4-20, 10-50 ma
Probe: Zero at zero DO, repeatable

Training: Factory-trained service technician is furnished to supervise initial operation of the system and instruct plant personnel in operation and maintenance. Membranes are simple to replace.

Options: W & S RC-1 Remote readout and calibration unit
Strip chart single pen recorder (multipoint type)
For multipoint systems: W & S Model S-6 switching box, plus the proper number of probes (max. cap. - 6 probes).

Materials and Design:
1) Cleaner-agitator is made of silicone rubber and may be set to provide continuous wiping of membrane under extreme fouling conditions, as in the presence of oil and greases.
2) Membrane: 2 mil Teflon - life about 1 month when used with cleaner-wiper
3) Supporting electrolyte: Potassium Iodide - 325 ml (solution used: 50 mg KI/100 ml)
4) Pb anode: Minimum 430 sq cm exposed to electrolyte

Other: Connections and mounting: Extension cords available as follows
a) two water proof cords - 2-conductor for power, one 4-conductor for signals
b) Y-adaptor and one 6-conductor power cable
Mounting holes provided for fastening to standard 1" pipe (Pipe mounting fixtures are available)

References

1) Weston and Stack Design Manual - Monitoring and Control of Dissolved Oxygen in Activated Sludge Systems
2) Weston and Stack Bulletin 3000 - Continuous Oxygen Monitoring: Dissolved Oxygen Analyzer

Cost*

Analyzer:	W & S Model 3000-1-A (or 3000-1-B)**	$700
	W & S Model A40 Probe Comes with a supply of 24 membranes	335
	W & S Model A-25 cleaner-agitator-sampler	355
	W & S Model RC-1 Remote readout and calibration unit (optional)	300
	Standard 25 ft Y-adaptor 6-conductor cable unit (Lengths up to 2,000 ft are feasible)	90
	Maintenance kit for probe includes complete set of o-rings, 24 membranes (1 mil & 2 mil), 32 oz. of electrolyte, a fill screw washer kit, fill-cap assembly, and membrane holder assembly.	70
	Agitator maintenance kit: O-rings shaft, sleeve bearing, thrust button & washer kit, grit seal & impeller wiper assembly.	50
	Special Mounting Bracket, including standard lower and upper mounting plates	125
	Current output recorder (Optional)	75
	Instruction Manual for operation and maintenance provided. Additional manuals	5.50

* Price breakdown is informational only. Products are priced and sold on a systems basis only including start-up, etc.

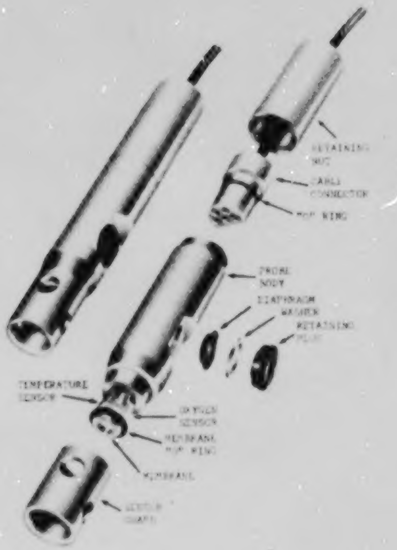
** A - Denotes enclosure is a JIC Box
B - Denotes enclosure is a Relay Rack
1 - Denotes a single channel system

Remarks	Direct contact of cleaner-wiper with membrane is required in the presence of oil or grease. Conductors carrying probe signal need not be shielded. Long conductor lengths are feasible. Separate recorder output calibration adjustment. Information obtained from manufacturer's literature or supplied by manufacturer on request.
Address	Rexnord Instrument Products 446 Lancester Avenue Malvern, PA 19355 Attn: William Wilkins–Market Manager or Edward Woytowicz–Sales Manager

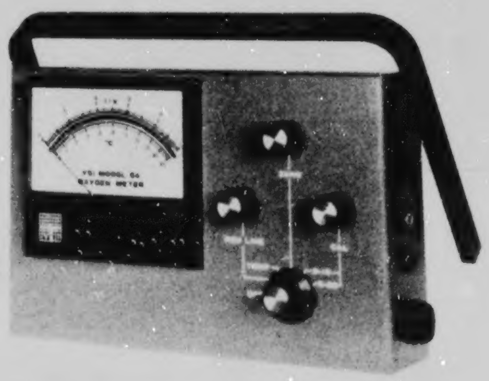
H2O-BIO
Field: DO
YSI 1
Sept. 1975

Dissolved Oxygen Analyser

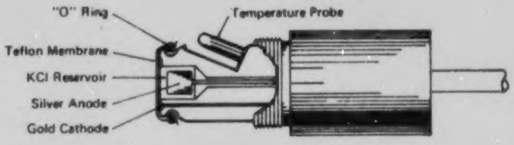
YSI Model 54A


RETAINING NUT
CABLE CONNECTOR
"O" RING
PROBE BODY
DIAPHRAGM WASHER
RETAINING PLUG
TEMPERATURE SENSOR
OXYGEN SENSOR
MEMBRANE "O" RING
MEMBRANE
SENSOR GUARD

YSI 5739 Dissolved Oxygen Probe



YSI Model 54A Dissolved Oxygen Meter


"O" Ring
Temperature Probe
Teflon Membrane
KCl Reservoir
Silver Anode
Gold Cathode

Class	Field/Lab/Portable
Categories of Water	Fresh/Waste
Principle of Operation	The YSI oxygen probe is a Clark type polarographic electrode system consisting of an annular gold cathode imbedded in a lucite block, and a silver anode recessed in a central well. The interior is filled with an aqueous solution of KCl. A thin Teflon membrane permeable to gases stretched across the end of the sensor isolates the sensor elements from the environment. When a suitable polarizing voltage of 0.65 to 0.8 volts is applied across the cell, oxygen will be reduced at the cathode, causing current to flow in an amount proportional to the partial pressure of oxygen at the membrane surface. Since oxygen is consumed at the gold cathode, the oxygen pressure inside the membrane is effectively zero, and the force causing oxygen to diffuse through the membrane is therefore proportional to the absolute pressure of oxygen outside the membrane. Thus a linear relationship is established between cell current and external oxygen pressure. Electrode reactions: Anode $2Ag + 2Cl^- = 2AgCl + 2e$ Cathode $1/2O_2 + H_2O + 2e = 2OH^-$
Minimum Detectable Sensitivity	0.05 ppm on 0-10 scale 0.10 ppm on 0-20 scale
Range	0-10 and 0-20 ppm scales 0-5 and 0-10 ppm with YSI 5937 High Sensitivity Membrane
Interferences	Halogens, H_2S, NO_x
Multiparameter Capability	Temperature

Sampling

Method: In situ probe
Volume:
  Maximum Depth: 600 ft
  Minimum Depth: None
Maximum Temperature Input: 45°C
Collection Efficiency: Not Applicable
Maximum Number of Sample Sources: Unlimited

Performance

Accuracy:
  Meter: ±0.1 ppm on 0-10 scale; ±1% F.S. at temperature of calibration
  Temperature: ±0.7°C (including probe)
  Automatic Temperature Compensation: See under "Temperature Compensation"
  Amplifier and Circuit: ±0.05%
Readability: 0.05 ppm on 0-10 ppm scale; 0.10 ppm on 0-20 ppm scale; Temperature readable to 0.3°C
Reproducibility: Instrument temperature stability, 2% of reading for each 25°C change of instrument temperature
Linearity: cell current is directly proportional to oxygen pressure under fixed conditions.
Noise: Not Applicable
Lag Time: Not Applicable
Rise Time: 30 sec for 95%
Retention Time: Not Applicable
Fall Time: 2 min for 99% to zero
Zero Drift: Trimable to zero
Span Drift: Negligible between calibrations

Operation

Ambient Temperature Range:
  Probe: -2° to +45°C
  Instrument: -5° to +45°C with NiCd batteries (54 RC)
    +5° to +45°C with Hg batteries (54 BP)
Temperature Compensation: Automatic temperature compensation for membrane coefficient and solubility of oxygen in water:
  ±1% of reading within ±5°C span of probe temperature;
  ±3% of reading over entire range of -2° to +45°C probe temperature.
Relative Humidity Range: 0 to 90%
Calibration: Air or other standard of choice
Procedure: The probe, after air calibration, is lowered into the water sample which is stirred, or the probe is kept in motion. The DO and temperature are read directly in ppm and °C.
Unattended Period: Not Applicable
Maintenance: Battery service and probe service

Requirements

Power: 54 BP - Four 1.35 V mercury cells (ca 1000 hr)
  54 RC - Four 1.25 V Ni-Cd cells (3 yr life; recharge every 100 hr)
Weight: 2.5 kg (5 lb)
Dimensions: Instrument - 25.5 cm x 9 cm x 16.5 cm (10" x 3-1/2" x 6-1/2")

Features

Output: Recorder 0 to 125 ± 15 mV
Training: Minimal - a few minutes of operator training are required
Options: Model 54 RC is powered by rechargeable batteries and contains a built-in charger operable on-line or on batteries.

Model 54 BP uses disposable Hg batteries (1000 hr life). It may be converted to a rechargeable model by means of a kit.

Model 51 A - similar to above, but has a salinity correction dial and can be read out in % saturation.

See also "Cost" under "Options"

YSI 5988 Carrying Case

YSI 5075 Calibration Chamber With
YSI 5739 Dissolved Oxygen Probe

YSI Model 51B Dissolved Oxygen Meter

YSI Model 54ARC Dissolved Oxygen Meter with YSI 5492A Battery Pack and YSI 5739 Dissolved Oxygen Probe Mounted in YSI 5795 Submersible Stirrer

References "YSI Dissolved Oxygen Meters," May 1972

Cost

Model 54A BP Oxygen Meter	$450.00
Model 54A RC Oxygen Meter (117 Vac 50-60 Hz Battery Charger)	480.00
Model 54A RC-230 Oxygen Meter (230 Vac 50-60 Hz Battery Charger)	510.00
Model 51B Oxygen Meter	355.00
Accessories:	
YSI 5775 Probe Service Kit, includes 0.5M KCl, membranes, replaceable o-rings	6.00
YSI 5075 Field Calibration Chamber	57.50
YSI 5776 High Sensitivity Membranes (15 pcs.)	6.00
YSI 5791 Submersible Stirrer, 50' lead (For longer leads place "X" after the part number, add $20.00 plus $0.35/ft. over standard length	201.00
YSI 5492A Battery Pack, including two 6 Vdc batteries	50.00
YSI 5988 Carrying Case	55.00
Probes:	
YSI 5739 Oxygen Temperature Probe	110.00
Order leads separately; 6 std. lead lengths:	
5740-10	29.00
5740-25	46.00
5740-50	57.50
5740-100	69.00
5740-150	95.00
5740-200	103.00
YSI 5720 Self-Stirring BOD Bottle Probe (117 Vac 50-60 Hz Stirrer)	275.00
YSI 5720-230 Self-Stirring BOD Bottle Probe (230 Vac 50-60 Hz Stirrer)	310.00
YSI 5450 Non-Stirring BOD Bottle Probe	140.00

Remarks Available only from YSI franchised dealers. List provided upon request.

Address

Yellow Springs Instrument Company
Box 279
Yellow Spring, OH 45387
(513) 767-7241
Attn: Dick Horn

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FOR
BIOCHEMICAL OXYGEN DEMAND

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INTRODUCTION

The early recognition of a relationship between the presence of microorganisms and organic matter in waters and their utilization of oxygen provided the impetus for the development of the present standard analytical procedure known as the *Biochemical Oxygen Demand (BOD)* test. (See Section 1. for a quantitative definition of BOD.) For more than 60 years BOD has been used to measure the presence of growth-supporting organic substances in aqueous solutions. First recommended in 1912 by the British Royal Commission on Sewage Disposal (Ref. 1) as a standard test of the purity of river waters and sewage effluents, the *5-day BOD test* was ultimately adopted in preference to the then current chemical (4-hour permanganate) test as the most sensitive quantitative indicator of organic pollution. Of all laboratory processes the BOD test came closest to reflecting actual in-stream conditions of oxygen depletion (Ref. 2). For example, in its study the Commission found that while chemical oxidation of either filter or tank effluents with potassium permanganate ($KMnO_4$; Section 3.3.1) might yield similar oxygen demand (OD) values, BOD analyses invariably resulted in much higher OD values for tank effluents. Consequently, the 5-day BOD test was adopted as "the most trustworthy chemical index of the actual state of a stream". It was further observed that if the BOD analysis was ≤ 4 ppm*, the stream would not show any apparent signs of pollution. Based on this maximum value for BOD (4 ppm), rivers were classified by the Commission according to their degree of pollution:

Table 1
(from Ref. 3, p. 131)
Royal Commission classification of rivers

Approximate 5-day BOD (ppm)†	Classification
1	Very clean
2	Clean
3	Fairly clean
5	Doubtful
10	Bad

†The Royal Commission used an incubation temperature of 18.3°C (65°F). The standard temperature now used is 20°C.

For a clean stream (BOD 2 ppm) providing a minimum of 8-fold dilution with clean water, it was calculated that the maximum BOD of sewage effluent should not exceed 20 ppm (Ref. 1). This maximum permissible figure was derived from the following considerations and the application of the law of mixtures:

Assuming the maximum safe BOD value for a stream to be 4 ppm, if

x = 5-day BOD (ppm) of the sewage effluent,

y = 5-day BOD (ppm of the stream just above the outfall (2 ppm), and

z = dilution factor (8) = the ratio of stream water to effluent moving past the outfall; then, from the law of mixtures,

$$4\ (z + 1) = (x \times 1) + (y \times z)$$

$$4\ (8 + 1) = x + 16$$

$$\therefore x = 20$$

Hence, assuming the arbitrary criterion of 2 ppm BOD for the above "clean" stream, the BOD of the sewage effluent may not exceed 20 ppm.

Biochemical Oxygen Demand defines the respiratory needs of a biologic community over a specified period of time, usually five days, expressed as mg/l of oxygen consumed. Microorganisms obtain their energy for cellular synthesis by the oxidation of organic substances available to them in the aquatic environment. Equation 1 depicts a typical aerobic respiration process using a biodegradable carbonaceous substance, glucose, as the energy source:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6\ CO_2 + 6H_2O + \text{energy} \qquad \text{(Eq. 1)}$$

Other energy sources function similarly to produce energy and the corresponding oxidative degradation products of the material utilized in the process. In waters containing relatively large amounts of organic substances, bacteria will consume most of the available oxygen. Most natural waters also contain algae populations which contribute to the BOD via their cellular processes or by functioning as degradable organic matter. The presence of algae can result in misleadingly high BOD values because of their increased oxygen demand (OD) in the dark resulting from their respiration.

A plot of BOD vs. time (Fig. 1) for waters polluted with organic wastes typically has a steep initial slope which decreases gradually, plateauing as the *ultimate oxygen demand* value is approached. The curve is best expressed by Equation 2 below:

---

*Currently, the c.g.s. system of units (mg/l) is preferred to ppm. The latter terminology is used here for reasons of historical accuracy.

$$y = L(1-10^{-k_1 t}), \qquad \text{(Eq. 2)}$$

where

y is the BOD at time t
L is the ultimate oxygen demand when organic oxidation is essentially complete
k_1 is a rate constant, and
t is the time elapsed from the onset of oxidation.

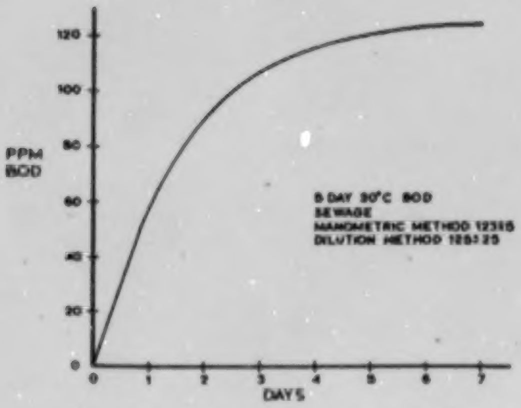

Figure 1. Rate curve, sewage (Ref. 52).

The *oxygen depletion curve* described in Equation 2 is related to the standard bacterial growth curve (Equation 3):

$$N_t = N_0 e^{kt}, \qquad \text{(Eq. 3)}$$

where

N_0 is the initial number of bacterial cells,
N_t is the number of cells at time t,
e is the natural logarithmic base, and
k is a growth constant.

The leveling off which occurs in the 5-day BOD curve (Fig. 1) parallels the exhaustion of initial biodegradable substrate in the sample.

1. Definition

Biochemical Oxygen Demand (BOD) is defined as "the quantity of oxygen required for biological and chemical* oxidation of water-borne substances under conditions of test" (Refs. 3, 4, 42). The BOD test (Section 7) is an empirical procedure used to determine the relative oxygen requirements of waters such as plant effluents, municipal waste waters, and receiving waters. It is widely used in the measurement of *waste loadings* in sewage treatment facilities. The *BOD removal* ability of a waste treatment facility is regarded as a measure of its functional efficiency.

Standard BOD test conditions include dark incubation of the sample at 20°C for a specified time -- frequently 5 days (Ref. 41). Since the complete *stabilization* of some wastes may entail impractically long incubation times, the 5-day incubation period has been universally adopted in the standard BOD procedure used by water analysis laboratories (Ref. 7). BOD measurements are usually reported in mg/l (preferred units) or ppm.

In the case of some industrial wastes, it is best to obtain an oxidation vs. time curve, particularly if one wishes to convert the data obtained from one incubation period to another. The assumption that all BOD rates follow simple exponential (first order) kinetics can lead to serious error (Ref. 7).

2. Factors Influencing BOD

Because the BOD determination is a biochemical test which depends on bacterial activity, it is not unexpectedly susceptible to error from a number of sources. Weston (Ref. 8) indicated that a minimum of 18 variables may influence the BOD test appreciably. In the following sections some of the most important of these factors will be discussed.

2.1 Temperature

The rate at which a biodegradable substrate is utilized by organisms in a biological system is temperature dependent. This stems from two factors:

1) The temperature dependence of chemical reaction rates in general, as described by the Arrhenius equation:

$$k = Ae^{-E/RT} \qquad \text{(Eq. 4)}$$

Here, k is the rate constant in reciprocal time units and

A = constant
E = energy of activation
R = gas constant, and
T = absolute temperature.

2) The effect of temperature on the rate of diffusion of substrate to the organisms in-

volved. This diffusion effect will not be considered here: for further information the reader may consult Refs. 9 and 10.

The Arrhenius equation was first proposed in 1889 to describe simple chemical reaction rates and was later extended by him to more complex biochemical systems. Here the activation energy E in Equation 4 denotes the overall activation energy for the organism(s) in a given system. The differential form of Equation 4 is also known as the van't Hoff equation:

$$\frac{d(\ln k)}{dT} = \Delta E/RT^2 \qquad \text{(Eq. 5)}$$

where k, E, R and T represent the values previously indicated for the Arrhenius equation (Eq. 4).

Temperature effects on the rate of substrate utilization have also been expressed in terms of *rate ratios* for substrate utilization -- the so-called *Q_{10} value*. This is simply the ratio of the substrate utilization rate for any temperature T to the corresponding rate at temperature T-10°. From the logarithmic form of Equation 5 one may infer the value $Q_{10} = 2$ in thermobiological reactions -- i.e., for every 10° rise in temperature the rate of reaction should double. This is known as the *van't Hoff rule* (Ref. 11). Thus, given the activation energy E of a biosystem, the Q_{10} value may be calculated. For example, using the E-value 14,200 cal/M for *E. Coli* (Ref. 12) and assuming that this value holds for the complex enzymatic reactions which occur in this system, the Q_{10} value obtained between 20 and 30°C is 2.23 (see Fig. 2(a).

It should be emphasized that the van't Hoff rule is a simple rule-of-thumb, to be applied cautiously. Used in this manner it generally furnishes a conservative estimate of the Q_{10} value (Ref. 13).

Streeter and Phelps (S-P) in their study of factors related to oxidation and re-aeration in the Ohio River (Ref. 14) developed the empirical expression below:

$$\frac{K'}{K} = \theta^{(T'-T)} \qquad \text{(Eq. 6)}$$

where θ is a thermal coefficient. K and K' are reaction velocities at temperatures T and T', respectively. For the average value of $\theta=1.047$ adopted by S-P, a Q_{10} value of 1.58 was obtained (Fig. 2(b)) is a comparison of rate-temperature curves obtained using the Arrhenius expression and the S-P formulation.

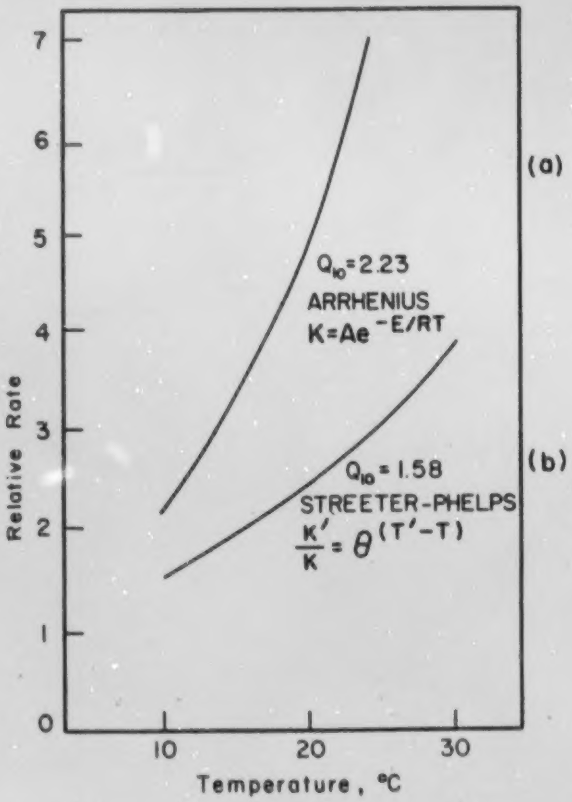

Figure 2. Rate temperature relationship (Ref. 9).

The S-P equation has been commonly employed to predict changes in reaction rate with temperature. However, as has been indicated (Section 11.1) the assumption of first order dependence of reaction rate on substrate is invalid. Busch concluded that the *soluble* component of substrate in a BOD bottle has been utilized within ca. 24 hours (Ref. 15). This reaction follows the bacterial growth curve, plateauing when the substrate has undergone complete conversion to energy and cellular materials. Respiration of the microbial population continues beyond this plateau stage, with cellular materials as substrates. Following the plateau, oxygen uptake is still partially contributed by the bacterial population, but it is attributed primarily to the growth of zooplankton which feed on the bacteria. Fig. 3 illustrates graphically the correlation suggested between utilization of substrate and microbial growth in a BOD bottle. On the basis of this picture, the original substrate system is depleted when the plateau appears. Thus the rate of substrate utilization must be calculated on prior data. This explains the failure of the BOD curve to follow first order kinetics throughout. Phelps did in fact recognize the discrepancy and pointed out that it was indeed reasonable for the BOD curve to mimic the bacterial growth curve (Ref. 16).

Since the Arrhenius equation was originally developed for thermochemical reactions of the type occurring (enzymatically) within bacterial systems, Equation 4 is regarded as accurately descriptive of these biosystems. Starting with basic thermodynamic principles, Eyring also developed a slightly different relationship which agreed well in the moderate temperature range encountered in these biosystems.*

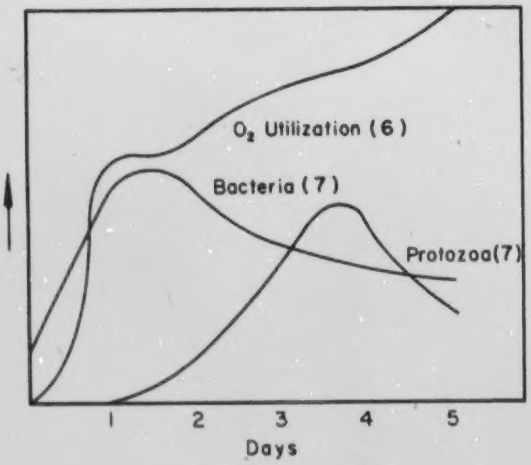

Figure 3. Changes in microbial-population with oxygen utilization (Ref. 9, p. 957).

For a system using sewage seed and glucose as the substrate, Busch (Ref. 9, p. 954) computed Q_{10} values on BOD progressions between 20° and 30°C to be about 1.35. This is well below the value predicted from the Arrhenius equation and from van't Hoff's rule for the system in question.

Only soluble substrate is utilized by bacteria; thus undissolved substrate must be solubilized before it can be converted either to energy or to new cellular materials. Once dissolved, the nutrient substrate must *diffuse* into the organism. Rate of diffusion of the substrate across the cell membrane is therefore an important temperature-dependent variable. Calculation of a Q_{10} value for glucose allowing for the effect of temperature on the diffusion coefficient of glucose in water results in a value of 1.3, which is in good agreement with the Q_{10} value calculated earlier on the basis of the experimental rate of substrate depletion (1.35). This is construed as evidence that the diffusion of substrate does actually constitute the rate-determining parameter related to the observed temperature dependencies (see Fig. 4).

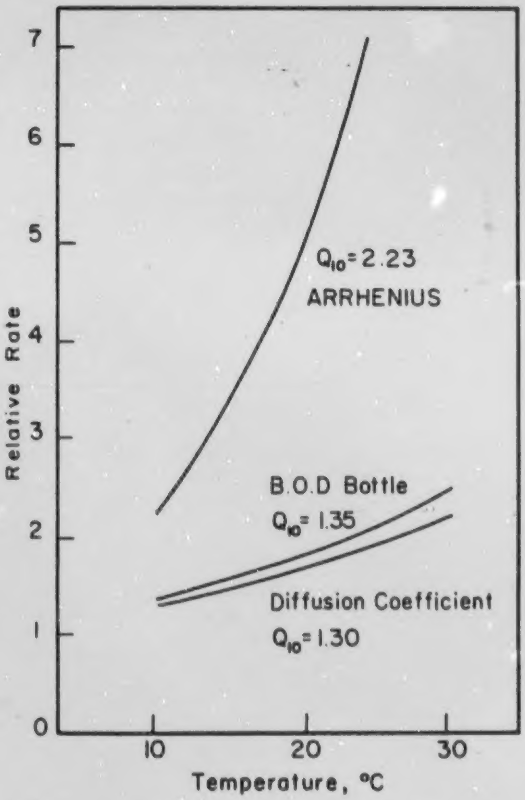

Figure 4. Rate temperature relationship (Ref. 9, p. 958).

Kehrberger et al have applied diffusion theory to a model bacterial substrate system and shown that:

---

*Reference II, Section 59c, "The Activated-Complex Theory of Reaction Rates" pp. 610-613 incl.; see also Sections 59a, b, pp. 606 ff, for a discussion of the Arrhenius equation and Collision Theory of Reaction Rates, respectively.

1) The effect of temperature on substrate utilization in a quiescent BOD bottle is indeed diffusion dependent.

2) Agitation or stirring of the sample during incubation results in a higher Q_{10} value by favoring *reaction limiting* conditions -- i.e., conditions providing maximum nutrient at the bacterial membrane.

Since a temperature change of as little as 1°C can produce a significant change in the BOD value of an effluent because the growth rates of bacteria and algae are strongly influenced by temperature, this parameter must be carefully controlled and accurately measured.

The standard temperature for BOD determinations originally recommended by the British Royal Commission on Sewage Disposal was 65°F (18.3°C). Subsequently this was raised to 20°C in conformity with the practice on the Continent and in the United States.

2.1.1 Thermal Loading and BOD

The term *thermal loading*, sometimes called "thermal pollution" when it is associated with detrimental effects on an aquatic system, refers to the increase in temperature resulting from some plant discharges (e.g., power plants). Interest in thermal loading stems from the fact that a temperature change may alter the environment of resident fauna and flora, and thus the BOD, sufficiently to affect the propagation and even the survival of biotic species. This results from the increased rates of biological reactions with increasing temperature (Section 2.1). An increase in thermal loading which exceeds the rate of heat dissipation for the surface waters, may result in permanent increases in temperature (and changes in BOD) over large areas. For further treatment of this subject, the reader is referred to Ref. 17, p. 95. See also Ref. 10, Chapter 37, p. 17.

2.2 Dilution Factors

The variation in the composition of tap water with location, as well as the current practice of chlorination, makes it an undesirable diluent for BOD analysis. It has thus become a standard practice to use distilled water prepared and stored according to recommendations in Standard Methods, 13th edition (Ref. 7).*

Dilution water for BOD determinations should be prepared by the addition of essential mineral *nutrients* (see Section 2.5) to high quality water. The quality of the water may be checked by incubation with *seeded* (see Section 2.6) samples. Organic contaminants may be detected by means of a *total organic carbon analyzer* (OD Instrumentation, Section 3.2). Experiments by Wheatland and Smith have shown that dilution water should be freshly prepared, preferably, or, if this is not feasible, it may be stored no longer than one week in thoroughly cleaned containers (Ref. 18).

The requirements of acceptable BOD dilution water include: 1) pH limits within which biota will grow; 2) a reasonable buffer capacity; 3) proper salinity; 4) absence of toxic substances, such as metallic contaminants, chlorine, or other growth inhibitors; and, finally, 5) the presence of a balanced and viable seed. Since it is frequently difficult to be certain that all these fundamental requirements are satisfied, Sawyer et al (Ref. 19) recommended the use of two primary standards, to be employed in the standardization of the methods employed. One standard is pure glucose (300 mg/l; 5-day BOD @ 20°C = 224 mg/l); the other, pure glutamic acid (300 mg/l; 5-day BOD @ 20°C = 217 mg/l). Standard Methods also recommends a glucose-glutamic acid check of the viability of dilution water (pp. 492-493).

The degree of dilution may also be a factor influencing the BOD value obtained (Ref. 42, pp. 816-820). Klein (Ref. 2) therefore suggested the use of several dilutions in a BOD analysis. The value obtained for the dilution showing approximately 50% DO depletion is then assumed to most nearly reflect the BOD of the sample. For some industrial wastes BOD is so largely a function of dilution (because of the presence of inhibitors -- see Section 2.3 below) that it can no longer be employed as a reliable test. In such an instance it is best to turn to a chemical method such as the standard dichromate test for the presence of organic substances (Refs. 3, 4) or the 4-hour permanganate test (Ref. 2, pp. 124, 129-30).

2.3 Toxic Substances and Inhibitors

When either the sample or the dilution water contains substances such as chlorine or metals capable of inhibiting or preventing bacterial growth, the magnitude of the errors introduced in the BOD test may render it worthless.

The presence of mineral acids or alkalis can have a significant effect on bacterial activity, and strongly acid or alkaline samples should be brought within a pH range of 6.5-8.3 before *seeding* (Section 2.6).

Toxic metals such as Cu, Pb, or Hg inhibit bacterial growth even when present in low concentrations. Copper is the worst offender in this respect and should be limited to <0.01 mg/l to avoid marked depression of BOD. For this reason a glass still is recommended in the preparation of dilution water (Ref. 7, p. 4).

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*Ref. 7, inside front cover. See also Ref. 4, Section 1193. Hereafter Ref. 7 will be identified simply as Standard Methods.

A "sliding BOD" value -- i.e., an apparent increase in BOD with sample dilution -- is diagnostic of toxicity in the sample.

According to one report on the toxicity of industrial wastes (Ref. 20) to the BOD dilution test, Hg toxicity increased only slowly for Hg values between 0.02-0.20 mg/l, but the curve rose steeply thereafter, and the BOD value was reduced to zero, for a Hg concentration of ∿2.0 mg/l.

As little as 0.1 mg/l of Cu or Zn was found to depress the BOD of sewage significantly, with copper the worse offender (when compared with zinc) for concentrations ranging all the way from 0.1-10 mg/l. For example, at 1 mg/l Zn lowers the BOD value by ca. 17%, but the effect of Cu at this concentration is nearly twice that of the Zn (33%) (Ref. 20). In a study on the effects of Cu and $CrO_4^=$, Placak et al (Ref. 21) reported that Cu and Cr ($CrO_4^=$) markedly inhibit BOD processes in concentrations as low at 0.01 mg/l Cu and ≥ 0.3 mg/l Cr (as ($CrO_4^=$). For 0.01 mg/l Cu a 5% depression in the BOD value was observed; at 0.05 mg/l, Cu lowered the value as much as 23%.

The findings on chromium BOD toxicity as a function of valence state and form of the Cr are somewhat contradictory, with Coburn (Ref. 22) indicating that trivalent Cr does not function as an inhibitor in the BOD test, whereas the Research Committee Report cited previously (Ref. 20) implies that trivalent Cr has a greater toxic effect thatn $CrO_4^=$ in the range of 1.0-10.0 mg/l Cr as measured by the standard BOD dilution procedure. In the presence of 0.9 mg/l Cr ($CrO_4^=$) the BOD was lowered about 20%. More recently, the NTAC report has concluded that there is no appreciable difference in the toxicity of Cr^{+++} and Cr^{+6}, at least where fish are concerned (Ref. 40, p.86).

Biochemical oxidation of organics is retarded by as little as 0.1 mg/l Pb (Ref. 23). Similarly it has been shown that the oxygen uptake rate for activated sludge is inhibited by a large number of metal ions (Cd^{++}, Cr^{+++}, Cu^{++}, Ni^{++}, Zn^{++}) in concentrations ranging from 1-100 mg/l (Ref. 24). These findings are summarized in Table 2 below.

Table 3 illustrates the effect of Cu on a BOD analysis as shown by comparison of the value obtained with a 4-hour permanganate test of the same stream. Here the very low BOD/$KMnO_4$ ratio (see Section 3.3.1) is indicative of the toxic inhibition of BOD by Cu.

Table 2

Toxicity of Metal Ions as Measured by Inhibition of O_2-Uptake in the BOD Test

Ion	Conc. (mg/l)	% Reduction of BOD	Reported by or worker	Reference
Cr^{+++}	0.01	5	Placak, Ruchhoft, & Snapp	21
	0.05	23	"	21
	1.0	33	Research Committee on Toxic Industrial Wastes	20
Zn^{++}	1.0	17	"	20
Cr^{+6} ($CrO_4^=$)	0.9	20	"	20
Hg^{++}	0.02-0.2	Conc'n-dependent inhibition	"	20
	2.0	No O_2 uptake		
Pb^{++}	0.1	Inhibition	Kalabina	23
Ni^{++}	1.0	"	Dawson & Jenkins	24
Cd^{++}	1.0	"	"	24
Cr^{++}	1.0	"	"	24

Table 3

Analysis of Stream Water Containing Organic Matter and Copper

		Concentration, mg/1
pH value		7.1
3 min permanganate value		14.2
4 hr permanganate value		64.6
Nitrite nitrogen		nil
Nitrate nitrogen		4.0
Ammoniacal nitrogen		0.7
Albuminoid nitrogen		0.26
BOD (5 days, 20°C)		4.3
Copper (settled sample)		1.6
Copper (shaken sample)		5.8
Suspended solids	mineral	30.0
	volatile	81.0
	total	111.0
Total solids		437.0

Adapted from Ref. 2, p. 132.

Thus, waters containing industrial wastes may give very misleading results in the BOD test, and the previously mentioned chemical methods are best employed in their analysis.

Saline waters generally yield low BOD values. Gotaas (Ref. 25) has stated that the biochemical oxidation rate of sewage is greatest for low concentrations of sea water (up to 25%). Grindley and Wheatland (Ref. 26) account for the BOD changes with salinity by variation in activity and numbers of *nitrifying* (see Section 2.4) bacteria. Because of this variability, BOD is not the method of preference in the determination of the extent of organic pollution in saline waters. This parameter is best assessed by chemical methods.

2.4 Nitrification*

Sewage effluents which are undergoing an incipient nitrification process manifest abnormally high 5-day BOD values which may be misleading. This is brought about by the consumption of additional oxygen, over and above that which may be attributed to *carbonaceous OD*** in the nitrification process. Lockett has cited an instance in which the 5-day BOD of a sewage effluent analyzed at 31.4 mg/1 contained only 9 mg/1 from carbonaceous sources, and remaining 22.4 mg/1 being utilized in the conversion of NH_3 to nitrate + nitrite (cited in Ref. 2, p. 125):

$$NH_4^+ + 3/2\ O_2 \xrightarrow[\text{bacteria}]{\text{nitrite-forming}} NO_2^- + H^+ + H_3O^+ \quad \text{(Eq. 7)}$$

$$NO_2^- + 1/2\ O_2 \xrightarrow[\text{bacteria}]{\text{nitrate-forming}} NO_3^- \quad \text{(Eq. 8)}$$

Figure 5 is an idealized illustration of the type of curve obtained

a) for the case of purely carbonaceous BOD, and

b) where nitrification is also involved.

Figure 6 illustrates the effect of temperature on the onset of the nitrification process in the BOD progression.

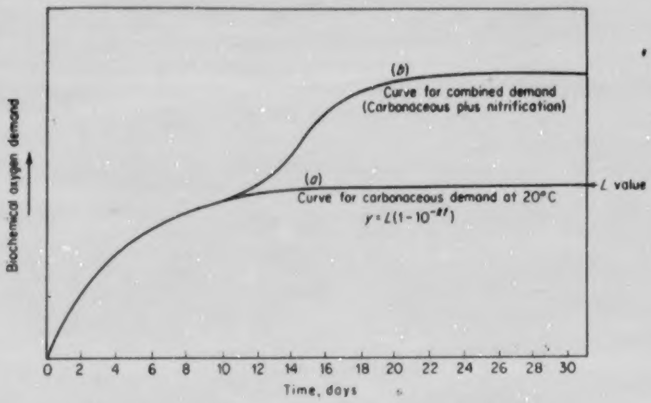

Figure 5. The BOD curve. a) Normal curve for oxidation of organic matter. b) The influence of nitrification. (Ref. 5).

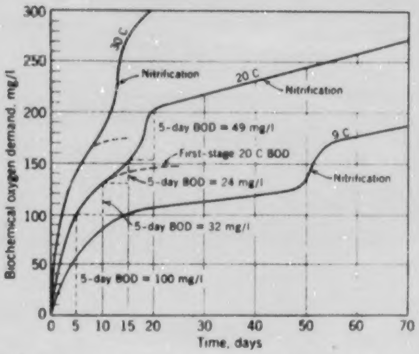

Figure 6. Progress of biochemical oxygen demand (BOD) at 9, 20, and 30 C. (Ref. 10)

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*Bacterial oxidation of ammonia and organic nitrogen compounds to inorganic nitrites and nitrates

**OD of organic carbon constituents present in the sample.

A number of methods have been employed to prevent this early onset of nitrification:

1) Destruction of nitrifying bacteria at 60°-80°C by flash pasteurization.

2) Chlorination of the sample to remove nitrifying bacteria followed by a treatment with Na_2SO_3 to remove excess chlorine.

3) Acidification of the sample to pH 2 to 3: this suppresses the nitrification process in the sample which must now be neutralized prior to BOD analysis.

After one of these three procedures is used to destroy the nitrifying bacteria, the sample may be diluted with water which has been seeded with settled domestic sewage known to be free of nitrifying bacteria.

4) Another method which suppresses nitrification without affecting the oxidation rate of carbonaceous materials was originally reported by Abbott (Ref. 27). This entails treatment of the sample with methylene blue. The addition of 6 ml of the dye (.05% aq. solution) for each liter of dilution water used eliminated errors due to nitrification. Dissolved oxygen was then determined using the Rideal-Stewart modification (see H2O-DO, Section 2.23) before and after the 5-day incubation period.

Unfortunately, none of the methods of nitrification control listed is completely satisfactory.

Nitrification can be of appreciable importance when effluents from an *activated sludge (AS)* plant, which contains much ammonia but little nitrate, and those from a biological filtration plant (rich in nitrifying bacteria), are juxtaposed. Stones (Ref. 2, p. 126) has observed that such mixed effluents may have a greater BOD value than would be predicted from their individual contributions. Table 4 illustrates the BOD-enhancing effect of such mixtures. This increase in BOD in the mixture may be explained on the basis of nitrification in the AS effluent (oxidation of the NH_3) by nitrifying bacteria originating in the filter effluent. Since this increases DO depletion, it is quite conceivable that two effluents which have separate BOD values well within the allowable range will, when juxtaposed, result in excessive DO depletion to the detriment of resident biota in a stream.*

2.5 Nutrients

Bacterial growth is dependent on an adequate substrate supply of mineral nutrients. While C, N, P and S are the most important essential elements, traces of minerals containing Fe, Ca, Co, Cu, K, Mg, Mn, Mo and Zn also appear to be required by most bacteria (Ref. 28). Nearly 40 years ago Lea and Nichols (Ref. 29) determined BOD on sewage and industrial wastes with both plain and supplemented bicarbonate dilution water, and concluded from their experiments that low BOD values would be obtained with certain wastes unless sufficient mineral nutrients -- in particular N and P --

Table 4

BOD of Mixtures of Activated Sludge Effluents and Filter Effluents from Plants Treating the Same Sewage

Activated sludge (Sheffield bio-aeration) effluent % by volume	Filtration plant effluent % by volume	BOD of mixture ppm
0	100	12.6
10	90	16.0
20	80	18.8
30	70	20.2
40	60	19.6
50	50	18.4
60	40	17.0
70	30	14.4
80	20	12.0
90	10	7.8
100	0	6.0

(Ref. 2, p. 126)

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*Such an enhancement of BOD due to juxtaposition of effluents does not present a serious problem in the U.S. where both filter and AS plants are usually operated under non-nitrifying conditions.

were available to satisfy the bacterial nutritional requirements. For example, they found that paper mill wastes diluted with water containing $Ca_3(PO_4)_2$, $MgSO_4$, KH_2PO_4, and $(NH_4)_2SO_4$ gave BOD values 2 to 5 times as high as those same wastes analyzed using unsupplemented dilution water.

In the case of pea canning wastes (high in N and P), the use of supplemented dilution water made no significant difference. Lea and Nichols' work indicated that the presence of a 0.2-0.5 mg/l of N and ca. 0.02 mg/l P would result in satisfactory BOD determinations. Sawyer and coworkers (Ref. 30) have demonstrated deficiencies in N or P or both in certain industrial wastes. Thus, cotton *kier* liquor is low in N, while brewery wastes are deficient in both N and P; tannery wastes are rich in N but P-deficient. In all cases where deficiencies exist, low BOD values may be expected unless these deficiencies are compensated in the dilution waters. For this reason, the standard dilution water now used contains essential supplementary nutrients. Although most natural stream waters probably contain sufficient mineral salts for the purposes of BOD analysis, those streams composed primarily of industrial effluent may pose analytical problems.

2.6 Seeding

For most sewage wastes and a few of the industrial wastes (e.g., those from the dairy industry) and for natural waters, the essential flora are already present and inoculation with bacteria will therefore not normally be required. However, chlorinated effluents require seeding after Cl_2 neutralization, and most industrial wastes, including strongly acid or alkaline effluents requiring neutralization before BOD analysis, will be deficient in the essential bacteria. To make up this deficiency, fresh settled sewage or sewage effluent is added to the dilution water. This type of seed has been shown by Sawyer et al (Ref. 19) to vary with the source of the seed when tested on pure organic compounds of known BOD. These variations in the character of the inoculum have been attributed to differences in the ratios of bacteria and protozoa in the seed source, and Zehnpfennig and Nichols (Ref. 31) demonstrated that, after filtration of the inoculum through a suitable sintered glass filter to remove the protozoa, reproducible BOD values can be obtained for the primary standards regardless of the source of the seed. High-BOD sulfite waste liquors from the digestion of wood chips with $Ca(HSO_3)_2$ solution (to produce pulp for paper) give unsatisfactory BOD results when standard seeding methods are employed (Tyler and Gunther, Ref. 32), but yield satisfactory results with a filtered soil extract as the inoculum.

Sewage effluents are not always a suitable inoculum for industrial wastes (Ref. 7, p. 490) -- in particular those which contain organic compounds resistant to oxidation by domestic sewage seed, or when the BOD is much less than

Table 5

Effect of Seed Type and Quality of BOD of Standard Glucose-Glutamic Acid Solution

Type of Seed	5-day Seed Correction *mg/l**	Mean 5-day BOD *mg/l*	Standard Deviation *mg/l*
Settled fresh sewage	>0.6	218	±11
Settled stale sewage	>0.6	207	±8
River water (4 sources)	0.05-0.22	224-242	±7-13
Activated-sludge effluent	0.07-0.68	221	±13
Trickling filter effluent	0.2-0.4	225	±8

*Section 1.6.1

(Ref. 7, p. 493)

2/3 of the *dichromate value* (see COD Section 2.1.1). In these circumstances the use of specially *adapted seed* is recommended, preferably obtained from the effluent from biological treatment of the waste itself, or from waters receiving it at a locus 2-5 miles below the discharge point. In the absence of these sources of adapted seed, it may be developed by continuous aeration of a large volume of water and by daily inoculation with small increments of the waste in question, along with domestic sewage or soil, until a suitable microbial population has been obtained (see Ref. 7, Section 219 3h).

The quality of the seed, dilution water and analytical technique employed (as well as the analyst!) should be checked periodically. The recommended procedure is described in Ref. 7, Section 4a-9. Table 5 illustrates the effect of seed type and quality on the BOD value obtained, using a standard glucose-glutamic acid test solution.

2.7 Anaerobic Organisms

In the presence of predominantly anaerobic bacteria from such sources as digested sludge, septic sewage or river muds, or the supernatent liquor from sludge digestion tanks, there is a lag of two or more days, so that the BOD values obtained are unusually low (see Fig. 7). This BOD-lag period results from the initially high concentration of the anaerobic species which do not require free (dissolved) oxygen for growth, but may utilize oxygen-containing compounds present for their metabolic processes. Ultimately as the concentration of anaerobic substrate decreases, the rates of the aerobic processes overtake and exceed the anaerobic rates, and the BOD curve "takes off".

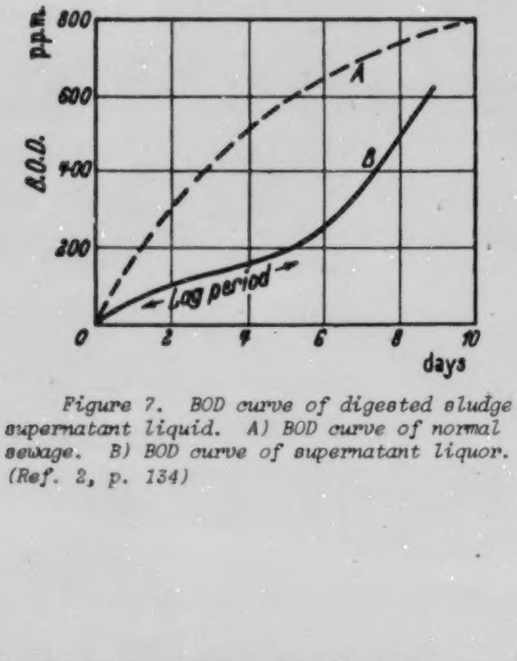

Figure 7. BOD curve of digested sludge supernatant liquid. A) BOD curve of normal sewage. B) BOD curve of supernatant liquor. (Ref. 2, p. 134)

2.8 Other Factors Influencing BOD

In addition to the sources of error and reasons for variability of BOD results reviewed in Sections 2.1 through 2.7 , many other variables appear as minor factors influencing this parameter. As an example, the presence of ferrous and ferric salts, nitrites and sulfites will interfere in the standard 5-day BOD test. Even a variation in bottle size, with its concomitant effect on the ratio of internal volume/surface may affect bacterial activity. A more complete discussion of the numerous minor errors appears in Ref. 33.

3. Relationship of BOD to Chemical OD Methods

Oxygen demand is also measured by a number of chemical procedures, each of which will be treated separately in later sections. However, a brief survey of the concepts involved should be helpful in clarifying such interrelationships between the chemical and biological measurements as do exist.

The BOD test has a biological basis in that it measures the amount of oxygen utilized during the oxidation of organic matter by aerobic bacteria under certain prescribed conditions (5 days @ 20°C). The difference between the initial and final concentrations of dissolved oxygen (DO, see H2O-DO Section of this Volume; also Ref. 7) in mg/l is taken as a measure of the BOD of the sample.

*Chemical Oxygen Demand (COD)** tests, such as the dichromate test (Ref. 7, p. 495) and the 4-hour permanganate test (Ref. 2, p. 120) constitute rapid analytical methods of chemical oxidation occurring under test conditions; they are useful in the estimation of the OD of organic carbon present in a sample. A more detailed discussion of COD may be found in the following chapter of this volume.

Thus, both BOD and each of the chemical methods play a significant role in the assessment of organic pollution; each method is concerned either with oxygen utilization of organic constituents or, more directly, with the actual amount of organic carbon present. Each method in its own way thereby furnishes an independent approximation of the quantity of organic matter present. Here, however, the resemblance between BOD and COD ends, for it is unreasonable to expect that the quantity of oxygen utilized in the course of metabolic processes of aerobic bacteria will correspond to that involved in a high-temperature chemical oxidation-reduction reaction. Factors which are operative in BOD (see Sections 2.3-2.7, inclusive) may have little or no influence on the chemical oxidation of organic constituents, and to some extent the converse is also true, as will be shown later in our discussion of chemical parameters.

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*Chemical oxygen demand (COD) is defined as "the amount of oxygen (in mg/l) consumed under specified conditions in the oxidation of organic and oxidizable inorganic matter in waste water, corrected for the influence of chloride." (Ref. 17, p. 214).

3.1 Nitrogenous Wastes

In general BOD remains the most sensitive test for nitrogenous organic pollutants which resist complete chemical oxidation; these include dairy and food processing wastes, farm drainage and sewage. BOD constitutes the principle test of the *strength* of sewage and industrial wastes -- i.e., the oxygen required to stabilize these wastes. In Table 6 below the resistance of ammonia and organically bound

Table 6

Analyses of Nitrogenous Organic Waste Waters

	Farm drainage	River polluted by dairy wastes	River polluted by sewage*	Unsatisfactory ** sewage effluents			Unsatisfactory** dairy effluent
pH value	7.2	7.0	6.8	7.4	7.1	6.8	7.2
3 min permanganate test ppm	3.0	1.0	1.0	6.8	4.4	5.0	4.5
4 hr permanganate test ppm	10.0	4.6	3.8	18.0	14.2	10.0	10.9
Nitrite nitrogen ppm	nil	nil	nil	nil	trace	nil	nil
Nitrate nitrogen ppm	nil	nil	nil	nil	1.5	nil	nil
Methylene blue stability test	Failed	Failed	Failed	Failed	Failed	Failed	Failed
	4 hr	18 hr	18 he	4 hr	18 hr	18 hr	4 hr
	(H_2S)	(H_2S)	(H_2S)	(H_2S)	(H_2S)	(H_2S)	(H_2S)
BOD (5 days, 20°C) ppm	39.0	60.0	12.9	39.6	40.9	32.5	76.0
Ammoniacal nitrogen ppm	--	0.10	0.92	--	--	--	--
Albuminoid nitrogen ppm	--	0.86	0.24	--	--	--	--
Dissolved oxygen, % of saturation	--	37	9	--	--	--	--

* Stream bed showed signs of sewage pollution (e.g., sewage fungus).

** "Unsatisfactory" here denotes undiluted sewage with a BOD >20 ppm. (Data derived from Ref. 2, p. 130)

Table 7

BOD & COD Analyses of Citrus Wastes

Raw Citrus Waste				Citrus Activated Sludge Effluent			
5-Day B.O.D. (p.p.m.)	Standard Methods C.O.D. (p.p.m.)	Colorimetric C.O.D. (p.p.m.)	Visual Comparison C.O.D. (p.p.m.)	5-Day B.O.D. (p.p.m.)	Standard Methods C.O.D. (p.p.m.)	Colorimetric C.O.D. (p.p.m.)	Visual Comparison C.O.D. (p.p.m.)
1,296	2,290	2,450	2,375	4.0	45	55	—
1,330	2,310	2,500	2,375	6.7	55	70	—
1,400	2,295	2,350	2,250	5.0	66	70	50
1,630	2,330	2,475	2,355	6.1	52	70	50
1,705	2,285	2,500	2,355	5.7	42	65	50
1,565	2,240	2,375	2,375	6.6	51	70	50
1,385	2,300	2,490	2,375	3.4	34	30	50
1,410	2,270	2,375	2,375	3.6	26	60	50
1,220	2,175	2,350	2,250	5.8	20	60	25
1,680	2,300	2,350	2,375	3.0	31	40	25
Average							
1,462	2,280	2,422	2,346	5.0	42	59	44

Ref. 34, p. 898

N to oxidation is illustrated by the absence of nitrates and nitrites in the samples tested. It should be noted that the dye methylene blue was uniformly successful in suppressing the nitrification step in all wastes examined. Further experimental verification of the superiority of the 5-day BOD method for these wastes is obtained by a comparison of the 4-hour permanganate values with the 5-day BOD values. Thus, while the BOD analyses clearly indicate the presence of organic pollutants, the $KMnO_4$ test fails to reflect quantitatively the actual organic pollution in these streams. The divergence between BOD and the chemical method is particularly great in the case of stream pollution by dairy wastes.*

3.2 Non-nitrogenous Wastes

For non-nitrogenous wastes use of the COD method with acid dichromate oxidant generally yields higher values than BOD, since it is a measure of total oxidizable organic material present, without regard to its biological availability. Table 7 illustrates this point for the case of citrus wastes measured by the standard dichromate procedure which entails titration of excess reagent with ferrous ammonium sulfate in the presence of an o-phenanthroline indicator. In each case, the third and fourth columns represent rapid colorimetric variants of the standard COD method, with measurements made after only 10 minutes of refluxing (Ref. 34). Table 8 gives ratios and statistical correlations for BOD vis à vis the three COD procedures.

3.3 BOD-COD Ratios

Because of the time-consuming nature of the BOD test, attempts to correlate this biological parameter with the faster chemical methods are ongoing. Historically these led to the examination of BOD-permanganate ratios (see Section 3.3.1 below). More recently they have taken the form of BOD-dichromate ratios and the examination of the *Oxygen Demand Index (ODI)* as a rapid estimate of BOD.

3.3.1 BOD-Permanganate Ratios

For crude domestic sewage, the 5-day BOD-permanganate (4-hour, N/80 $KMnO_4$) ratios are of

Table 8

Ratios and Statistical Correlations of Analyses by Different Procedures (Ref. 34, p. 898).

C.O.D. Comparison	Raw Citrus Waste			Citrus Activated Sludge Effluent		
	Ratio	Correlation Coefficient	No. of Samples	Ratio	Correlation Coefficient	No. of Samples
Std. Methods C.O.D. vs. B.O.D.	1.56	0.4346*	23	[illegible].40	0.4699*	20
Colorimetric C.O.D. vs. B.O.D.	1.66	0.4669*	23	[illegible].80	0.4496†	17
Visual C.O.D. vs. B.O.D.	1.60	0.2639†	19	8.80	0.6780‡	15
Colorimetric vs. Std. Methods C.O.D.	1.06	0.3113†	31	1.40	0.4305*	24
Visual vs. Std. Methods C.O.D.	1.03	0.0973†	26	1.05	0.6255‡	21
Colorimetric vs. Visual C.O.D.	1.03	0.0325†	26	1.34	0.4218†	21

* Significant correlation at 5 per cent level.
† Correlation not significant at either 1 or 5 per cent levels.
‡ Significant correlation at 1 per cent level.

Table 9

Comparison of BOD and 4 hours permanganate figures for different types of sewage (Birmingham) (Ref. 2, p. 135).

Name of works	*Character of sewage*	*5-day B.O.D.* p.p.m.	4 h *permanganate value* p.p.m.	*Ratio B.O.D.: permanganate value*
Barston . .	Domestic	236	59	4
Coleshill. .	Domestic	229	76·5	3
Yardley . .	Industrial*	222	120	1·8
Saltley . .	Industrial*	264	159	1·66

* Contains large proportion of metallic trade wastes.

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* Standard Methods currently employs catalytic oxidation of organics with acid dichromate solutions as the chemical method of choice. This gives closer agreement with carbonaceous BOD in the absence of nitrogenous OD, but is subject to limitations which will be discussed in greater detail in the COD section.

the order of 2 to 4 (BOD/$KMnO_4$). With carbohydrate-rich or nitrogen-rich wastes (dairy and food processing) the ratio may exceed these values. This ratio may be adversely affected by industrial chemical effluents containing non-nitrogenous organics, metals, etc. In Table 9 above the BOD-$KMnO_4$ data for four different sewage effluents are compared. The corresponding ratios for sewage containing industrial effluents are consistently lower than for domestic sewage. The significance of this divergence is that the $KMnO_4$ figure indicates the *amount of organic pollution* requiring treatment, whereas the BOD value is a measure of the *ease of biological oxidation*. A low BOD/$KMnO_4$ ratio (e.g., <1) therefore indicates that the effluent is more resistant to biochemical oxidation (Ref. 35).

Inhibition effects on BOD of industrial wastes were further shown by Goldthorpe and Nixon (Ref. 36) who mixed chemical wastes containing Fe, organics and dyestuffs with sewage in varying ratios. They obtained BOD/$KMnO_4$ ratios which varied all the way from 0.2 for chemical wastes alone to over 3.0 for sewage alone.

In the absence of industrial wastes, sewage and tank effluents give relatively high BOD/$KMnO_4$ ratios (>1). However, a properly purified sewage effluent or effluent of good quality containing industrial organic nitrogenous wastes, will generally have ratios of <1, indicating a BOD value which is lower than the corresponding permanganate value.

Table 10

Winter T_bOD of Davis Municipal Sewage (Test Series 1) (Ref. 38).

1 Test Date	2 Theoretical Initial COD_m	3 Mixture Initial COD_m	4 Measured Cell COD	5 Initial COD_s	6 Endpoint COD_f	7 ΔCOD	8 Sewage Dilution Factor	9 T_bOD	10 Measured Sewage COD
2/17	585	584	293	287	36	251		279	318
2/24	618	598	367	251	33	218	0.9^{-1}	242	279
3/5	791	746	681	110	62	48		53	122
3/25	372	363	188	184	49	133	0.918^{-1}	145	200
3/26	534	524	296	238	60	178	0.9^{-1}	198	264
4/2	658	626	330	328	38	290		322	364

Table 11

Summer T_bOD of Davis Municipal Sewage (Test Series 2) (Ref. 38).

1 Test Date		2 Theoretical Initial COD_m	3 Mixture Initial COD_m	4 Measured Cell COD	5 Initial COD_s	6 Endpoint COD_f	7 ΔCOD	8 Sewage Dilution Factor	8a T_bOD	9 Average T_bOD	10 Average Measured Sewage COD
6/26	1	333	316	144	189	34	155	0.9^{-1}	172	173	210
	2	461	437	272	189	32	157		174		
6/28	1	-	417	292	125	23	102		113	117	147
	2	-	703	564	139	30	109		121		
7/2	1	527	520	291	236	27	209		232	235	266
	2	813	817	570	243	28	215		239		
7/9	1	256	258	141	115	20	95		105	105	128
	2	399	358	285	114	20	94		105		
7/16	1	353	357	147	206	37	169		188	188	229
	2	505	433	299	206	37	169		188		

3.3.2 BOD-Dichromate Ratios

In a recent investigation of a rapid BOD method based on a differential COD technique (Ref. 37, see Section 11.3.2) Schroeder and co-workers (Ref. 38) calculated the TBOD (Total Biological Oxygen Demand) for municipal sewage from COD data. Tables 10 and 11 above list their TBOD and COD values for winter and summer months, respectively. As in the case of citrus wastes cited previously (Table 7, p. 1), BOD/p. 11 dichromate ratios are <1, i.e., COD values are consistently higher than BOD, since they reflect organic (and inorganic) oxygen demand without regard to biological activity or toxicity factors.

Similarly, OD analyses on primary effluent from Midland, Michigan, show a COD/BOD ratio ➤ 1 (Fig. 8).

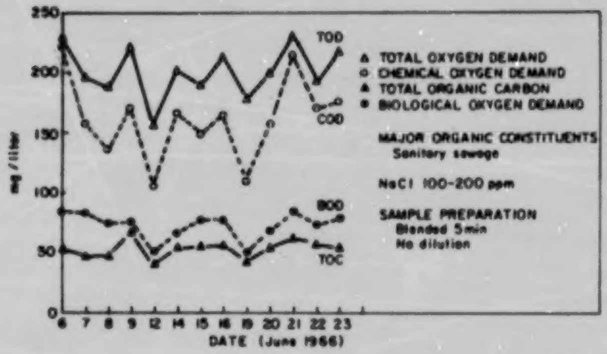

Figure 8. City of Midland primary effluent. Reprinted from Ref. 39, Vol. 4, p. 1470.

4. Limitations of the BOD Method

Some disadvantages of BOD as an indicator of organic pollution have already been noted under Section 2 in dealing with factors which influence BOD values obtained. In this section these limitations will be summarized briefly.

4.1 Time Factor

The standard BOD procedure is time-consuming at best. At worst, as in the case of nitrogenous compounds and inhibitors, the 5-day incubation period may yield misleading (low) results due to a lag or induction period before the biochemical oxidation process begins. Conversely, nitrification may lead to excessively high BOD values.

4.2 Validity

The test is of limited value when used to obtain OD values for surface waters, since it does not reproduce actual stream conditions. BOD is a *batch* or *discrete* measurement, executed under static aerobic conditions. Thus such continuous variables as stream velocity, temperature and the existence of anaerobic as well as aerobic areas in a dynamic stream situation are not accurately reflected by the BOD measurement.

4.3 Reproducibility

Because of the large number of variables which may influence the BOD test (see Sections 2 and ff), comparisons of BOD data are valid only for identical test conditions.

4.4 Metals and Toxic Inhibitors

Even in low concentrations the following metals are toxic to bacteria: Cu, Cr, Hg, Pb. Because of its dependence on bacterial growth, BOD is very vulnerable to the toxic effects of metals, whereas chemical methods are relatively insensitive to them.

4.4.1 Other BOD Inhibitors

Other *bacteriocidic** and/or *bacteriostatic** substances which may inhibit bacterial activity, and thereby result in low BOD values in the presence of organic pollution, include free chlorine, cyanides, formaldehyde (CH_2O), and phenols. Numbered among the important industrial wastes which may give low BOD results because of the presence of such inhibitors are those from gas, petroleum and chemical (phenols, formaldehyde, TNT, etc.) and plating industry wastes. In these instances, the BOD analysis is best replaced by a more suitable COD method such as the dichromate test (Refs. 3, 7).

4.4.2 Evidence for BOD Inhibition

When an apparent increase of BOD is observed within a series of increasing dilutions of a sample, the presence of a toxic substance or inhibitor is indicated.

*See glossary

4.5 BOD-resistant Organic Materials

The assumption that BOD is directly proportional in magnitude to the organic pollutants present is only approximately correct since there exist organic substances and partial degradation products, such as lignins, oils, and alkybenzenesulfonate type detergents which are strongly resistant to further biochemical oxidative degradation. These substances are not detectable via the standard BOD procedures, but their build-up in a stream may be nonetheless objectionable, either by virtue of their imparting undesirable physical characteristics (taste, odor, frothing, etc.) or because they are toxic.

Analysis of the supernatants from sewage sludge, septic sewage, or any liquor which has undergone initial *anaerobic* fermentation will invariably give a low 5-day BOD value. However, this is probably due to an initial lag period during which the changeover to aerobic fermentation occurs, and further fermentation of such samples beyond the 5-day limit is likely to show a rapid increase in OD. This phenomenon is illustrated in Fig. 7, and was discussed under Section 2.7.

5. Criteria

The report of the National Technical Advisory Committee (NTAC) (Ref. 40) does not specify allowable BOD values for various kinds of effluent. Clearly, BOD limits will vary with the intended use of the water. For public water supplies, "permissible criteria" are stated in terms of dissolved oxygen (≥ 4 ppm, monthly mean value); "desirable" criteria: near saturation (i.e., negligible OD present). The allowable BOD values for undiluted waste waters will vary with the nature of the waste treatment prior to discharge and stream dilution of the discharged effluent.

For further discussion of BOD in relation to the following subjects the reader should consult Ref. 40: aquatic life, p. 57; farm wastes, p. 132; irrigation water, pp. 118, 166; pulp wastes, p. 90; *Sphearotilue*, p. 51; supplemental irrigation, p. 175.

6. Summary and Conclusions

In summary, it may be stated that while BOD is still regarded by most sanitary engineers as the method of choice for determining organic pollution of waters, it is subject to a number or limitations and errors discussed under Section 4 as well as to additional parametric limitations (Section 2). Briefly, these are as follows:

1) BOD is temperature-sensitive and limited by the viable temperature range for the biota involved.
2) BOD measurement to be meaningful requires a mutually compatible substrate and bacterial population. In the case of a resistant substrate, a suitable seed may be developed (Section 2.6).
3) The BOD test must be conducted under non-nitrifying conditions.
4) The sensitivity of BOD to a large number of metal ions and other inhibitors serves as an indicator of the presence of toxic substances by virtue of the "sliding scale" of BOD -- e.g., the apparent increase in BOD with sample dilution.

These factors must be considered in any reasonable interpretation of BOD data.

Where BOD results are ambiguous, the data from this bioanalytical method should be compared with data obtained using chemical methods. Thus, when the 5-day BOD appears too low compared with the dichromate or permanganate analysis, each of the following possibilities may need to be considered:

1) A bacteriostat or toxic substance may be present.
2) Unsuitable seed, or seed requiring acclimatization may be the problem.
3) Biochemically oxidation-resistant substances may be resulting in low BOD values vis à vis the chemical ones.
4) Or, the presence of anaerobic bacteria may be causing a BOD lag. In any of these instances, examination of long-term BOD-rate curves can be illuminating (see for example, Figs. 7 and 8).

Despite its limitations, the BOD test by its very nature remains the most sensitive criterion of organic pollution and continues to serve as the principal pollution *indicator* for sewage and industrial wastes.

7. Five-day BOD: The Method

The BOD test is identified primarily with the standard laboratory procedure developed to measure water quality (Refs. 2, 3, 7). The sample of waste water and appropriate dilutions are incubated in the dark for five days @ 20°C. Reduction of DO content during the incubation period is taken as the measure of BOD of the sample (see Refs. 3, p. 117; 7, p. 489; 41). EPA recommends the BOD procedure described in the 13th edition of Standard Methods. The exact procedure used will depend on the nature of the sample and involves one of three methods:

1) Direct Method: For samples whose DO is <7 mg/l*, the sample is first aerated to near saturation (Ref. 3) and the DO** determined initially and after the 5-day dark incubation period at 20°C.
2) Unseeded Dilution Method: For waters with DO > 7 mg/l, the following procedures are recommended:
    a) Appropriate dilutions are prepared with O_2-saturated standard dilution water (Ref. 7a); or,
    b) Appropriately diluted samples are saturated with O_2 (Ref. 3).
3) Seeded Dilution Method: When the sample contains microorganisms capable of oxidizing the organic substrate present (as would be the case for domestic sewage or unchlorinated effluents), it is not seeded. However for samples likely to be deficient in microorganisms -- i.e., chlorinated effluents or those subjected to extremes of pH or temperature, a standard seed material is employed. This consists of settled domestic sewage stored at 20°C for 24-36 hours. Standard dilution water (Ref. 7a) containing 1 to 2 ml of this standard seed per liter is used as diluent for microorganism-deficient samples (Ref. 7, Section 219-3h). The preparation of adapted seed for organism-resistant industrial wastes has already been described (Section 2.6).

Dilution water which has been seeded should be used the day it is prepared.

7.1 Procedure†

If the pH of the waste sample is not between 6-8, it is first neutralized to pH 7 with the help of a pH meter (see this volume H2O-pH) or the use of bromothymol blue as an external indicator. It is then diluted as required (see below) with buffered distilled water containing 1 ml each of the following reagent solutions per liter of distilled water: phosphate buffer, $MgSO_4$, $CaCl_2$ and $FeCl_3$ solutions. It is essential that the dilution water be sufficiently buffered that the pH will remain constant throughout the dilution range.

For dilution water which is stored in the refrigerator prior to use, the phosphate buffer is not added until immediately before its use.

For diluting samples the dilution water, seeded if necessary, is carefully siphoned into a graduated cylinder to 1 to 2-liter volume avoiding entrainment of air. The desired amount of sample is then added, again avoiding aeration, and the solution is further diluted as required. Mixing is done with a plunger to avoid air entrainment. Two aliquots of the solution are then siphoned into separate BOD bottles. One is incubated in the dark at 20°C, the other analyzed for initial DO content. Incubation and analysis of blank dilution water is carried out simultaneously. Oxygen depletion on the unseeded dilution water should not amount to more than 0.1-0.2 mg/l. Dissolved oxygen analysis may be chemical (azide method; H2O:DO, Section 2.2.2) or by means of a membrane electrode (H2O-DO, Section 3.6).

Incubated samples are sealed tightly against air and should be water sealed, either by the use of a special water-seal bottle, or by inversion in a tray of water.

An alternate technique simplifies water sealing: it consists of measuring known aliquots into volumetric bottles or flasks which are then filled with sufficient dilution water that air bubbles are excluded on sealing.

The viability of the seed, when used, and/or the presence of toxic materials which act as growth inhibitors are detected by means of the glucose-glutamic acid check (Ref. 7, Sec. 219-4a7). A mixture containing 150 mg/l each of reagent grade glucose and glutamic acid provides a stabilized oxidation rate comparable to that obtained from municipal wastes.

7.2 Glucose-Glutamic Acid Check Procedure

All three variables (analyst, dilution water, and seed) may be checked as follows: 5 ml of the glucose-glutamic acid solution are diluted with seeded dilution water and incubated with a seed control @ 20°C for five days. The variation of glucose-glutamic acid BOD with seed type is illustrated in Table 5 of Section 2.6 (p. 9).

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*i.e., below the saturation value of DO @ 20°C.

** *Dissolved Oxygen*: see this volume H2O:DO, section 1.0 for factors influencing oxygen solubility.

†For preparation of standard solutions, dilution techniques, and other procedural details, the reader is referred to Ref. 7, Sec. 219, p. 489 ff.

Results obtained from sample dilutions with a residual DO content of ≥ 1 mg/1 after the 5-day incubation, and a depletion of ≥ 2 mg/1 are most likely to be reliable.

7.3 Seeding

The seeding of dilution water is described in greater detail in Standard Methods, 13th edition (Ref. 7), and in Traversy (Ref. 3). A general discussion is also included in Section 2.6 of this chapter. The seeding errors incurred in BOD measurements are considered in detail by Stack (Ref. 42).

7.4 Chlorinated Waters

Waste samples containing residual chlorine are allowed to stand 1 to 2 hours to dissipate the chlorine. For higher chlorine residuals*, the chlorine is destroyed by reduction with sodium sulfite solution (Na_2SO_3). The quantity of Na_2SO_3 required is determined as follows: a 0.1-1.0 liter aliquot of the sample is treated with 1:1 acetic acid or 1:50 H_2SO_4-H_2O solution and 10 ml KI solution containing 10 gm KI/100 ml solution. It is then titrated to the starch-iodine endpoint with Na_2SO_3 solution (0.025 N). The required volume of sulfite solution as determined above is then added to another waste aliquot and tested for residual Cl after 10 to 20 minutes. The necessary BOD dilutions are then prepared using seeded standard dilution water.

Several dilutions of the treated sample should be prepared to bracket the BOD value of the waste sample. The following dilution ranges have been recommended (Ref. 7): 1) high level industrial wastes, 0.1-1%; 2) raw or settled sewage, 1-5%; 3) oxidized effluent, 5-25%; and 4) polluted streams, 25-100%. For further discussion of samples requiring special treatment, the reader is again referred to Section 219 of Standard Methods, 13th edition.

8. BOD Versus IDOD

A number of substances are rapidly oxidizable by molecular O_2 and will therefore also deplete the water of DO. These include aldehydes, ferrous salts, sulfides and sulfites. Waste waters polluted with such reducing agents will show an *Immediate Dissolved Oxygen Demand (IDOD)*; the total OD is then the sum of this initial OD value plus the 5-day BOD. IDOD does not necessarily indicate that the oxidation by DO will be immediate; rather, these substances may merely react with the liberated iodine in the iodometric (Winkler) DO analysis (H2O:DO, Section 2.2):

$$2Fe^{++} + I_2 \xrightarrow{H^+} 2Fe^{+++} + 2I^-$$

Thus, they add to the apparent OD of the sample. IDOD is arbitrarily measured at 15 minutes. This is done by determination of the initial OD (usually zero) for the sample and the dilution water, and the OD for an appropriate dilution of the sample after 15 minutes. The difference between the initial DO and the DO after 15 minutes of an appropriate dilution is termed the IDOD of the sample.

9. Calculations of BOD

A. For the unseeded system,

$$\text{BOD (mg/1)} = \frac{D_1 - D_2}{P}, \text{ where} \qquad \text{(Eq. 9)}$$

D_1 = IDOD (i.e., DO after 15 minutes)

D_2 = DO of incubated sample, and

P = sample dilution, expressed as a decimal fraction.

B. For the seeded system,

$$\text{BOD (mg/1)} = \frac{(D_1 - D_2) - (B_1 - B_2)f}{P} \text{ where,} \qquad \text{(Eq. 10)}$$

D_1, D_2 and P are as defined under A, and

B_1 = DO of dilution of seed control prior to incubation,

B_2 = DO of dilution of seed control after incubation, and

f = ratio of seed in sample to seed in control

$$= \frac{\%\text{ seed in } D_1}{\%\text{ seed in } B_1}$$

$(B_1 - B_2)f$ = seed correction.

C. For the seeded system, if IDOD = 0 or not determined,

$$\text{BOD (mg/1)} = \frac{D_C - D_2}{P}, \text{ where} \qquad \text{(Eq. 11)}$$

$D_C = (DO)_O = D_O p + SP$ (time = 0)

D_2 and P are as defined under A.

S = DO of undiluted sample, and

p = fraction of dilution water used (expressed as a decimal).

D. For IDOD $\neq 0$,

$$\text{IDOD (mg/1)} = \frac{D_C - D_1}{P}, \text{ where} \qquad \text{(Eq. 12)}$$

D_C, D_1, and P are as defined previously.

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*i.e., residuals which persist beyond two hours; where this is suspected, the sulfite titration is done on an initial aliquot.

10. Precision and Accuracy

Precision was determined by analysis of a glucose-glutamic acid mixture in 34 laboratories, each with its own seed material. The geometric mean value obtained was 184 mg/l; the standard deviation, ±31 mg/l or 17%. A single analyst working in his own laboratory obtained a 5% precision (±11 mg/l for a BOD of 218 mg/l).

It is not possible to determine the accuracy of the BOD test, since there is no suitable standard for this purpose.

11. Alternatives to the 5-day BOD Test

The standardized laboratory procedure for determination of the oxygen requirements of effluents, polluted waters and waste waters as described in Standard Methods, 13th edition, is used primarily to assess the waste loads imposed on treatment facilities and their efficacy in coping with these imposed burdens, measured in terms of "BOD removal". Biochemical oxygen demand is widely used in the evaluation of sewage strength, process efficiency and effluent quality. However, in order to have any validity, the BOD test must be executed under carefully controlled conditions. It is extremely limited as a measure of the oxygen demand (OD) of surface waters and extrapolation of the results obtained to in-stream oxygen demands is not without hazard, since clearly the environment of the aliquot contained in a sample bottle has totally different biotal, oxygen, sunlight, temperature, and kinetic conditions. The information supplied by the test provides a "historical" record which is related to the organic components present at the beginning of the test, but it is seriously limited as a parameter of ongoing water quality control (Refs. 7 and 42).

A number of alternatives have been suggested in an attempt to overcome the uncertainties and shorten the duration of the BOD test (Refs. 37, 38, 42-45 inclusive). These will be discussed briefly in the following sections.

11.1 Energy Oxygen: Definition

As Stack (Ref. 42) has so aptly remarked, the "bottled" 5-day BOD system is "100% accurate in representing itself, but unreliable as a representation of the (dynamic) system from which the sample was taken." He has suggested an alternative approach to the problem of obtaining more current, and therefore, in his opinion, more useful BOD-*related* information based on the fundamental reactions involving *energy oxygen (EO)*.

Energy oxygen is defined as that part of the required oxygen which is utilized by biota in the synthesis of new cellular products or biologically stable organic substances. "Thus at the point where the original organic material no longer exists, oxygen consumption corresponds to energy oxygen and is equivalent to 10-40% of the *chemical oxygen demand (COD)* of the original organic material" (Stack, Ref. 42, p. 804). Incubation time for this process is of the order of one to two days. Long-term first stage *carbonaceous BOD* utilizes 60 to 80% of the total *Chemical Oxygen Demand (COD)* leaving behind relatively inert materials such as polysaccharides (Ref. 46) which are not readily susceptible to further breakdown. This takes 10 to 20 days. During this *cell stabilization* period ammonia is released via degradation of N compounds such as amino acids.

Bacterial *nitrification* (oxidation to nitrites and nitrates) may or may not occur at this stage. If incubation is continued beyond this stage, the ultimate value of BOD developed will represent essentially total oxidation of all C, H, and N *(ultimate OD)* (Ref. 47).

11.1.1 Energy Oxygen as a Biological Parameter

Early theoretical treatments of BOD have been based on the assumption of the occurrence of first order kinetics (see Introduction, p.2) within the BOD bottle, an assumption which has not withstood the test of everyday sanitary engineering practice (Refs. 6, 15, 48, 49). Stack (Ref. 42) therefore recommends discarding the questionable first order assumption and substituting the "actual occurrences in the BOD bottle." These are:

a) oxygen utilized in the energy reactions previously discussed (*energy oxygen - EO*), and
b) oxygen consumed in subsequent *endogenous reactions* which result in relatively stable organic end products.

Assuming that a method can be developed to determine EO rapidly, simply, and reliably, then biological cell production during that time may provide the basis for a calculated endogenous oxygen value. The sum of these two values (i.e., EO + endogenous oxygen) is the *stabilization oxygen demand* (Ref. 42).

Figs. 10 and 11 illustrate BOD curves for glucose and sodium acetate, respectively. *Ultimate carbonaceous BOD* is differentiated from the *stabilization OD* values in that the former value is defined as the oxygen required for complete conversion of organic carbon and hydrogen to CO_2 and water. This value is reached

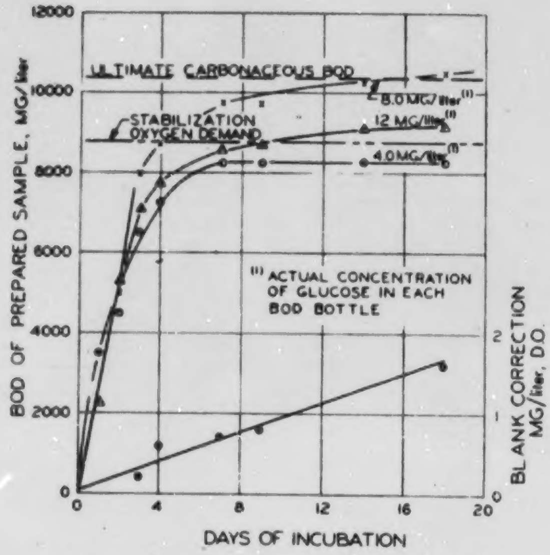

Figure 9. Biochemical oxygen demand, glucose. 10,000 mg/liter prepared sample.

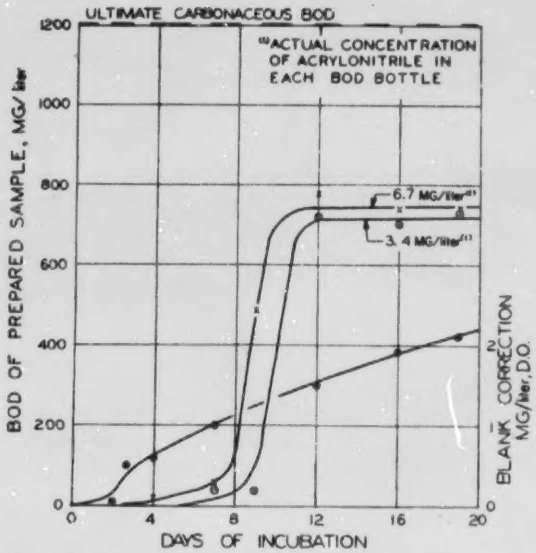

Figure 11. Biochemical oxygen demand, acrylonitrile. 670 mg/liter prepared sample.

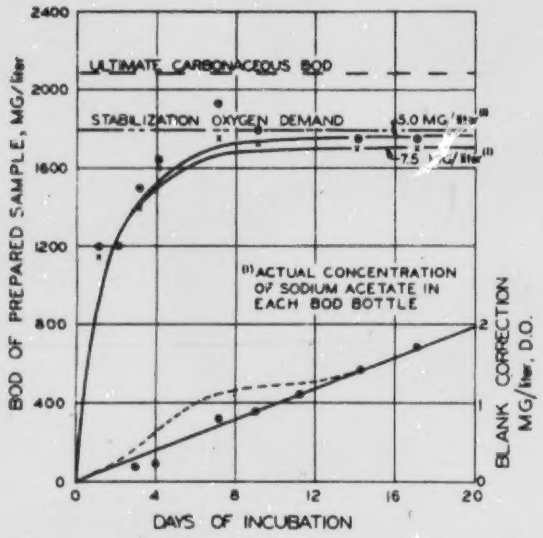

Figure 10. Biochemical oxygen demand, sodium acetate. 2,500 mg/liter prepared sample.

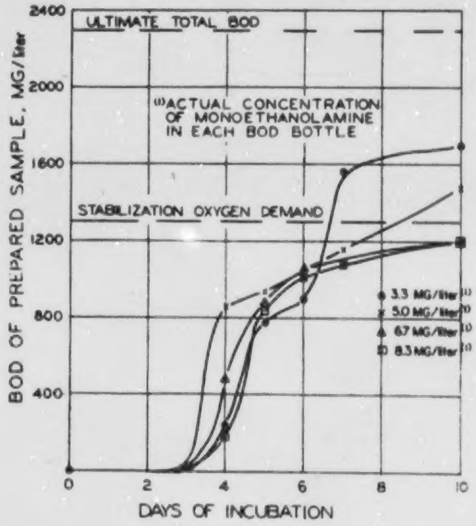

Figure 12. Biochemical oxygen demand, monoethanolamine. 1000 mg/liter prepared sample.

asymptotically whereas the stabilization OD is attained in a finite time (approximately 8 days for glucose, and 7 days for NaAc). For these simple (non-nitrogenous) examples the BOD curves appear to fit roughly first order kinetic expressions. However nitrogen-containing compounds (see Figs. 11 and 12) such as acryonitrile and monoethanolamine show poor correlation in the 5-day BOD test, exhibiting induction periods (*lag*) and concentration-dependent nitrification.

11.1.2 Measurement of EO

For the measurement of energy oxygen, the Warburg Respirometer (Fig. 13) is frequently employed (Ref. 43). In the respirometric method, oxygen consumption is measured as the difference between the values obtained for seed alone and for seed and sample. Net oxygen consumption at the endogenous stage (corrected for seed O_2 consumption) represents *energy oxygen*.

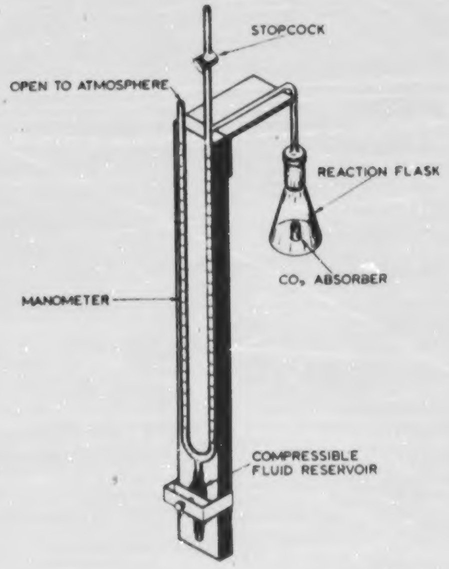

Figure 13. Diagram of Warburg apparatus.

Energy oxygen measurement has also been used as a parameter in biological activity studies (Refs. 43 and 50). It is an important concept in the clarification of bio-oxidation processes. An attempt to correlate EO values obtained from turbidity data (related to cell synthesis) with those gleaned from Warburg measurements has not been satisfactory (Ref. 51.)

11.2 STOD

Another approach is that of Vernimmen and coworkers (Ref. 44) who used the following procedure for *short term oxygen demand (STOD)* measurement. The O_2-uptake in a stirred, sealed system, seeded with a culture, was measured under endogenous conditions using a DO probe (see H2O-DO, Sec. 3.6). Introduction of the wastewater sample resulted in an increase in O_2-uptake, followed by a return to the endogenous state when the energy OD of the organic wastes had been removed. The net consumption of oxygen between initial and final endogenous states reflected the EO utilized by the waste (Fig. 14).

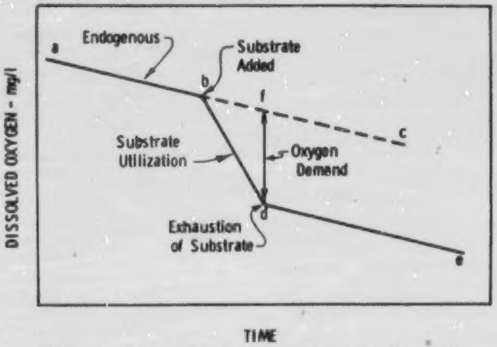

Figure 14. Short term oxygen demand. (from Ref. 44, p. 1006)

11.3 TBOD

Mullis and Schroeder (Ref. 38) applied the *mass culture aeration* technique of Hiser and Busch (Ref. 37) to the determination of the *TBOD (total biological oxygen demand)* of insoluble wastes. In a mass culture, the bacterial concentrations are much greater than in the usual BOD test, being of the order of several hundreds or thousands of milligrams of organisms per liter of the culture. The procedure involves separate chemical oxygen demand (COD) (Sec. 1.2) determination of the soluble substrate and of a washed mass culture of aerobic microbial organisms suspended in tap water. A mixture containing a known volume of each component is then aerated. Substrate utilization is traced by first analyzing *filtered* samples withdrawn periodically, employing the COD test. The point at which filtrate COD becomes constant is termed the *end-point filtrate COD (ef-COD)*. From it, TBOD is obtained using the following equation:

$$\text{TBOD} = \text{D.F.} \times \Delta\,\text{COD (mg/1)}, \qquad \text{(Eq. 13)}$$

where D.F. = dilution factor = volume of mixture/volume of substrate, and

ΔCOD = difference between initial COD and ef-COD.

Fig. 15 shows a typical curve: examination of the diagram reveals that a suitably selected substrate-culture ratio (*loading*) can insure a short completion time for the test.

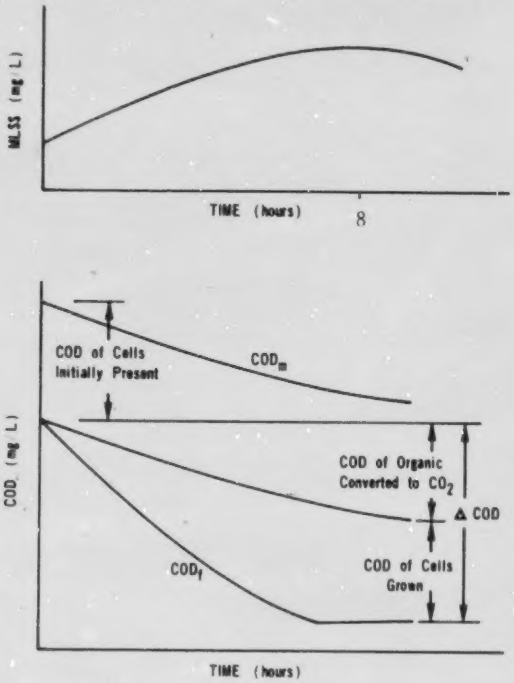

Figure 15. TBOD

The experiments of Hiser and Busch (Ref. 37) indicate that the TBOD test is accurate within ±10%. This is greater accuracy than afforded by the 5-day BOD test and therefore acceptable for use in process control.

11.3.1 Mass Culture Aeration Methods: General Considerations

In the mass culture TBOD test, it is the remaining soluble* carbon (food) present at any given time that is measured -- not oxygen uptake. Consequently, and unlike its importance in the 5-day BOD test, the fraction of food converted to cellular matter, i.e., the ratio of cellular material formed/CO_2 produced, is irrelevant here. The use of a 0.45 μ filter excludes new cellular material formed from the filtrate, since bacterial dimensions are generally >1 μ. Consequently there is no danger of confusing new organic carbon formed with that originally available. Only the chromate-oxidizable fraction of the *soluble* organic carbon is measured; and only that total amount of soluble organic carbon that is biodegradable by the culture used. Thus TBOD, unlike the 5-day BOD test, is a measure of the ultimate OD of the substrate.

When the TBOD test is applied to a mixed solid and soluble substrate, difficulties arise due to the difference in COD for the *MLSS (mixed liquor suspended solids)* and the filtrate moietiés. The modified test described above takes this difficulty into account in that the difference between the initial and final COD in the filtrate reflects the OD of the insoluble organics, and new cell synthesis, rather than TBOD. Substitution of this difference (Δ (COD)) in Equation 13 will then yield the TBOD value.

11.3.2 Δ COD**

Since most of the rapid procedures suggested as alternates to the 5-day BOD method are based on certain similar assumptions, a brief analysis of the salient points will be presented in this section. For simplicity the treatment will exclude from consideration any nitrification or non-bacterial processes.

Denote initial and final COD values as $(\text{COD})_o$ and $(\text{COD})_\phi$, respectively. Then

$$\Delta\text{COD} = (\text{COD})_o - (\text{COD})_\phi \qquad \text{(Eq. 14)}$$

$$(\text{COD})_o = \Sigma \text{ soluble carbon + seed + insoluble carbon}$$

$$= \Sigma\, SC_o + B_o + IC_o \qquad \text{(Eq. 15)}$$

$$(\text{COD})_\phi = \Sigma \text{ soluble carbon + seed + new cells + insoluble C}$$

$$= \Sigma\, SC_\phi + B_o + B_n + IC_\phi \qquad \text{(Eq. 16)}$$

$$\Delta\text{COD} = (\text{COD})_o - (\text{COD})_\phi$$

$$= SC_o + B_o + IC_o - [SC_\phi + B_o + B_n + IC_\phi] \qquad \text{(Eq. 17)}$$

For $IC_o = 0$, and COD determinations carried out on *filtrates* only, $B_o + B_n$ are eliminated, and ΔCOD reduces to:

$$\Delta\text{COD} = SC_o - SC_\phi \qquad \text{(Eq. 18)}$$

For $IC_o \neq 0$, and $B_o \approx$ constant,

$$\Delta\text{COD} = SC_o + IC_o - [SC_\phi + IC_\phi + B_n] \qquad \text{(Eq. 19)}$$

---

*Soluble material is defined as that which will pass through a .45 μ filter.

**This section is based on an analysis by J.J. Connors of the assumptions of the Mass Culture Aeration technique (private communication).

At time t,

$$(COD)_t = SC_t + IC_t + B_t \text{ (where } B_t = B_o + B_n)$$

For t = 0, $(COD)_o = SC_o + IC_o + B_o$

From Mullis et al (Ref. 38), the COD for substrate plus new cells is:

$$(COD)_s = [SC + IC + B_o + B_n] - B_o \quad \text{(Eq. 20)}$$

For t = 0, $B_n = 0$, and Equation 20 reduces to

$$(COD)_{s,o} = SC_o + IC_o \quad \text{(Eq. 21)}$$

From Equation 19 above,

$$\Delta COD = SC_o + IC_o - [\overbrace{SC_\phi + IC_\phi + B_n}^{A}]$$

$$\Delta COD = (COD)_{s,o} - A \quad \text{(Eq. 22)}$$

At this point, Mullis et al make the following two assumptions:

1) All insoluble carbon is converted either to CO_2 or to new cells. Thus,

$$IC_\phi = 0, \text{ and} \quad \text{(Eq. 23)}$$

2) B_n (new cells formed) may be ignored, analytically, since they are not filterable, so that

$$\Delta COD = (COD)_{s,o} - SC_\phi, \text{ and} \quad \text{(Eq. 24)}$$

$$TBOD = [(COD)_{s,o} - SC_\phi] \times D.F. =$$
total biological oxygen demand.

This is identical with Equation 13.

In a recent article Gaudy and Gaudy (Ref. 45) argued that the use of the BOD test as a measure of "purification efficiency" was not defensible and recommended ΔCOD for this purpose. They pointed out that the purpose of biological treatment was the removal of biologically available organic matter, and that any method which measured this removal was acceptable. They further cited two measurement criteria: 1) the method must reflect the % *metabolizable* organic matter removed during treatment, and 2) it must be fast enough to be useful in dealing with any malfunction which results in a lower quality effluent in a treatment facility. Examination of the plot of a hypothetical system (Fig. 16) reveals the changes which would be observed when a system containing a biologically available organic substrate, S, is seeded with appropriate (i.e., *acclimated*) microorganisms. Microbial growth is shown as an increase in biological solids. The accumulated oxygen uptake, y, is a measure of the BOD of the system, and ΔCOD measures the amount of substrate removed. Dichromate digestion of organic matter to $CO_2 + H_2O$ measures total oxidizable organic matter in solution (COD). By a plot of the results of periodic analyses for solids (x), collected using the membrane filter technique, and a corresponding plot of COD determined on the filtrates, equivalent diagrams may be obtained experimentally. Oxygen uptake *(BOD exertion, y)* may be determined manometrically or by means of a sensor in the case of dilute solutions. This yields three vital parameters of the system: (a) the amount of solids present at a given time t, (b) the organic substrate (COD) present at time t, and (c) the oxygen uptake (BOD exertion) for the time in question. For the simplest system which contains *aerobic organotrophs* only (e.g., no nitrifying bacteria, etc.) oxygen uptake will measure carbonaceous BOD only. Where the slope of the curve y approaches zero, the *ultimate BOD* value, L_o, has been attained. As is clear from the diagram, O_2 uptake continues at the expense of the biological solids produced, long after BOD removal of the original substrate. The familiar "plateau" in

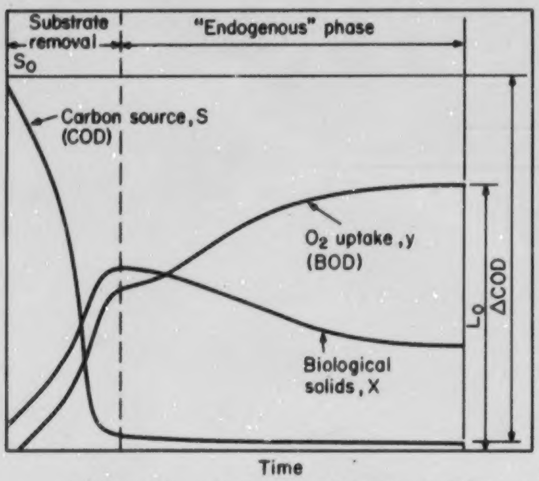

Figure 16. Generalized plot of substrate concentration, biological solids concentration, and oxygen utilization during exertion of biochemical oxygen demand. This figure shows the course of microbial growth (increases in biological solids, X) which would be observed if one placed a small inoculum (seed) of microorganisms in a vessel in the presence of a biologically available source of carbon (substrate, S) to which the microorganisms were acclimated. Also shown are plots of the accumulated oxygen uptake (BOD, y) and the total amount of organic matter remaining in solution measured by a general chemical test involving the digestion of organic matter to carbon dioxide and water in the presence of potassium dichromate under acid conditions, i.e., the chemical oxygen demand test. The total amount of substrate removed is ΔCOD. L_o represents so-called ultimate BOD; at this point the oxygen uptake has ceased. (From Ref. 45, p. 32.)

the BOD curve occurs when substrate removal is essentially complete and is often used as an indicator that this condition has been achieved.

If the curves in Fig. 16 are viewed from the standpoint of waste purification such as occurs in an *activated sludge (AS)* aerator, essentially similar reasoning may be applied: i.e., the carbon source is removed, biological solids build up, and O_2 is utilized in the process. The difference is that during the normal operation of an AS process, the *endogenous* phase reactions of the right hand side of Fig. 16 are not allowed to occur, since the solids are generally separated in the clarifier before the treated waste is discharged as effluent. The latter, depending on flocculation and settling efficiencies, will contain more or less of the non-metabolized organics (COD), but the biologically-produced solids will have been largely retained as sludge. The difference between influent and effluent COD is a measure of the organic matter removed in the aerator:

$$COD_{influent} - COD_{effluent} = \Delta COD \qquad \text{(Eq. 25)}$$

When ΔCOD is at a maximum value -- i.e., cannot be reduced further by biological means -- then ΔCOD becomes a measure of the amount of organic wastes available to the microorganisms in the system. This is often confused with BOD, but as may be seen from the diagram, L_0 (the *ultimate BOD* of the waste) is different from ΔCOD. Because a significant fraction of L_0 is exerted after original carbon removal has occurred, the oxygen-uptake of this fraction depends on the degree of aerobic digestion of the solids produced, and may be considerably more variable than ΔCOD. Thus, it would appear that ΔCOD is a more reliable test than the 5-hr BOD test or L_0. Since ΔCOD (as opposed to COD) is a measure of only that fraction of the waste which is *biologically available*, it may be used to estimate the organic BOD present, even in the presence of non-biodegradable COD. Thus, a waste may be high in lignins which are relatively inert biologically, but which are oxidized chemically in the COD test. Such a waste would have a high COD, but the effluent would not present any serious challenge, at least so far as DO depletion is concerned.

11.4 Parameters Related to Cell Synthesis

Since the synthesis of new cellular substances is the direct result of energy consumption, quantitative measurement of all syntheses is essential to ascertain the degree of biological activity. The suggestions of Busch and Myrick (Refs. 15, 48, 49) for the gravimetric determination of *suspended solids (SS)*, or the measurement of increased COD for the SS, presents difficulties where precipitates are already present, or where there is a low degree of synthetic activity by bacteria utilizing organic substances in dilute solution.

Production of new *deoxyribonucleic acids (DNA)* may also be used as a measure of new cell production. The method involves a differential technique and is unfortunately a slow and laborious one (Ref. 53).

Two other methods which have been used in cell synthesis measurements take advantage of biochemical oxidation-reduction processes. When 2,3,5-triphenyltetrazolium chloride (TPTZ-oxidized form) is reduced by diphosphopyridine nucleotide (DPN-reduced form), it forms the red-colored formazan. This reaction was used by Kun and Abood (Ref. 54) as an indicator of the viability of cells. Brodie reported that the reaction is a stoichiometric one under aerobic conditions (Ref. 55) and it has been used to measure biological activity in activated sludges (Ref. 56).

The production of ATP *(adenosine triphosphate)* has been related directly to bacterial growth, and is the intermediate in energy transfer for this process (Ref. 57). Thus ATP production and the reduction of TPTZ both offer promise in the measurement of cell synthesis reactions.

11.5 Utility of Alternatives

In the last analysis, biological activity can be quantitatively ascertained only through parameters which relate directly to such activity, i.e., cell production and/or O_2 consumption. However, the *indirect* relationship to biological activity of such parameters as COD and TOC *(total organic carbon)* often provide useful and rapid indicators for ongoing monitoring operations when used in conjunction with BOD measurements.

12. General Analytical Considerations

A BOD analysis may be concerned with 1) establishing the biosynthetic and oxidation reactions of a naturally existing population of microorganisms such as might occur in domestic sewage, or in a surface stream, or 2) the detection of organic substances which may provide the substrate for an *acclimated** culture of microorganisms.

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*See p. 9 and below; see also Standard Methods 13th edition.

Where a natural culture is employed, it should be checked for BOD activity with the standard glucose-glutamic acid substrate, as described in Ref. 7. Since a domestic source of sewage may contain inhibiting industrial wastes at times, the glucose-glutamic test is necessary to establish the viability of the seed source. In the case of the so-called *acclimated cultures*, the organisms are exposed to the organic substances which are not a normal food source (Refs. 2 and 7) and natural adaptation is allowed to occur.

12.1 Toxicity

When BOD fails to develop in the presence of an inoculum, it may be due to one of two factors; 1) materials resistant to bio-oxidation and/or 2) the presence of toxic substances in the sample.*

The procedure recommended for determining toxicity consists of a series of BOD tests over a wide dilution range. It is assumed that, where acute toxicity exists, bio-oxidation reactions are inhibited. However, masking chemical reactions which utilize DO may also be involved. It is therefore advisable to perform an *IDOD (immediate dissolved oxygen demand)* test. In addition, if organically polluted wastewaters fail to show an OD, an internal control in the form of a readily oxidized organic substance should be added to each dilution in the series (Ref. 58). For a further discussion of toxicity tests and interpretation of results, see Ref. 42, pp. 814-16.

12.2 Dilution

The procedure for preparing high quality dilution water is described in Ref. 7. Toxic inorganic cations are removed in the distillation process, or by the use of an appropriate ion exchange procedure. Organics, in particular the lower boiling ones, pose more of a problem. BOD dilution water may be checked by incubation with seed or by analysis using a *total organic carbon (TOC)* analyzer, which can detect as low as 0.2% (mg/l) of organic C (Ref. 59). In any event, dilution water is best checked for organic contamination prior to use.

As has already been indicated, low concentrations of organics are not easily removed from dilution waters. Among the methods used to accomplish this end are 1) pre-seeding and long (>1 week) incubation of dilution water prior to use; and 2) re-distillation with rejection of the first cut to eliminate low-boiling organics. Fig. 17 illustrates a still recommended for the latter procedure. The use of a blank correction may sometimes be essential for the meaningful interpretation of BOD data, according to Stack (ref. 42).

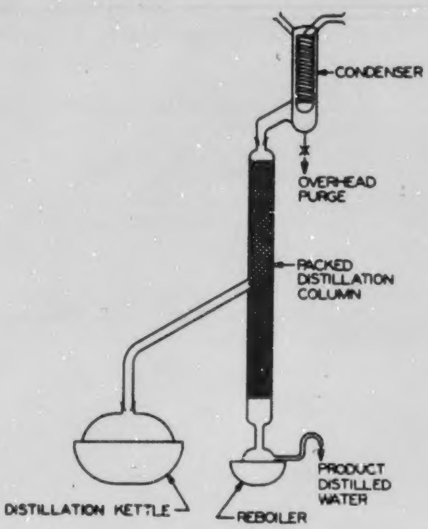

Figure 17. Water distillation apparatus (from Ref. 42, p. 817).

Interpretation of oxygen depletion results must consider at least the following factors: 1) "blank" oxygen consumption related to organic contaminants present in the dilution water; 2) the oxygen consumed by the seed itself plus any organic substances present in the seed inoculum; and 3) nitrification processes. In addition to these considerations, oxygen may be consumed in the (auto-oxidative) reactions of free radicals (Ref. 60) in solutions which are otherwise sterile.

12.3 Nitrification

Samples which have not been *biologically stabilized* may undergo long periods of carbonaceous BOD development without concomitant oxidation of nitrogenous materials to nitrates *(nitrification)*. However, where partial biological stabilization has occurred, nitrification (Sec. 2.4) may take place within the 5-day BOD test period, yielding confusing oxygen-consumption data. Such unadjusted data, if applied to problems such as the organic loading of a stream, or the efficiency of a bio-oxidation process, can be very misleading.

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*For acute toxicity tests see Ref. 4: 1973 Book of ASTM Standards, Vol. 23.

As the emphasis on water quality becomes greater, it will become more essential to determine the ultimate OD's of systems, isolating the carbonaceous and nitrogenous moieties. A number of techniques have been employed to deal with this problem; they have been discussed briefly in section 2.4 of this chapter. For a more complete discussion of these alternatives and additional references, the reader is referred to Ref. 42, Chapter 15 (pp. 820 ff).

In Figs. 9-12 (p. 19), the effect of concentration of substrate on nitrification indicates a correlation between sample dilution and the initiation of nitrification. Stack (Ref. 42) recommends that one approach to the problem would be to substitute re-aeration for sample dilution where nitrification is a problem. By the use of oxygen probes, the DO content can be monitored non-destructively, and the sample re-aerated at intervals as necessary (Ref. 42, p. 822).

12.4 Sampling

"...The prime requirement of all samples, regardless of the method of collection, is that they be representative....For in all cases, the quality of any investigation of an aquatic eco-system is no better than the sampling program used." (Ref. 61)

In general, the sampling methods and precautions employed for DO (H2O:DO, Sec. 2.1) analysis apply to BOD. See Ref. 4, Sec. D-510, for a discussion of sampling techniques.

12.4.1 Samplers and Sampling Locations

Samples for BOD determination are generally collected in narrow-necked glass-stoppered (G.S.) flasks of 200 to 300 ml capacity, with flared rims. Great care must be exercised in the collection of samples for BOD analysis to avoid agitation or post-sampling contact with air, in order to minimize the risk of oxygen exchange. The method of sampling is influenced by the source of the sample, the depth from which it is to be aliquoted, and even the method of analysis to be used. King (Ref. 61) suggests the use of special samplers such as the Kemmerer water sampler or the Nansen water bottle for the collection of all water samples to be used in the determination of DO, in order to avoid oxygen exchange between the sample and the atmosphere. Standard Methods (Ref. 7) recommends a Kemmerer-type sampler (Fig. 18) for all samples collected from depths of more than five feet. In the latter instance the sample is bled from the bottom of the sampler through a tube reaching to the bottom of a 250-300 ml BOD bottle. The bottle is filled to overflowing, then allowed to overflow for about 10 seconds, great care being exercised to avoid turbulence and bubble formation during the bottle-filling operation. Water temperature is recorded with the desired precision.

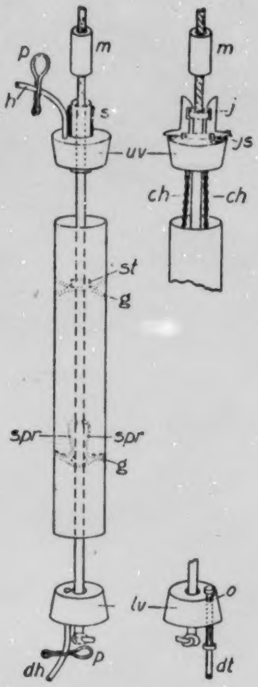

Figure 18. Modified Kemmerer sampler. Left: view of complete sampler with valves open. Top right: another type of construction of upper valve and tripping device. Bottom right: another type of construction of lower valve and drain tube. Key: ch--chain which anchors upper valve to upper interior guide; dh--rubber drain tube; dt--brass drain tube; g--interior guide fastened to inner surface of body of sampler; h--rubber tube; j--jaw of release; js--jaw spring; lv--lower valve; m--messenger; o-opening into interior of drain tube; p--pinchcock; s-upper release spring operating on horizontal pin, one end of which fits into groove on central rod; spr--spring fastened to lower internal guide and operating in groove on central rod to provide lower release; st--stop on central rod; uv--upper valve (from Ref. 7, p. 728).

The locations of sampling points for waste waters are best situated where homogeneous mixing is most likely (e.g., the downstream side of a hydraulic jump or weir). When a narrow, deep channel or a sewer is sampled, a grab sample, to be representative, should originate at approximately 1/3 the depth of the sample source. For wide channels sample collection points should be rotated across the channel width, and the flow velocity should be sufficiently great to avoid the deposition of solids. The creation of turbulence during sampling must be avoided, since this can result in a misrepresentative sample due to the loss of dissolved gases. It is very difficult to obtain a truly "representative" sample of such a heterogeneous mixture as, say, oil-polluted wastewater. Nevertheless the collection of a composite sample can result in analytical data which do give a reasonable profile of the waste waters sampled.

Figs. 19 and 20 are a sketch and a schematic diagram of an automatic sampler (Ref. 17, pp. 124-5) used in sewer sampling.

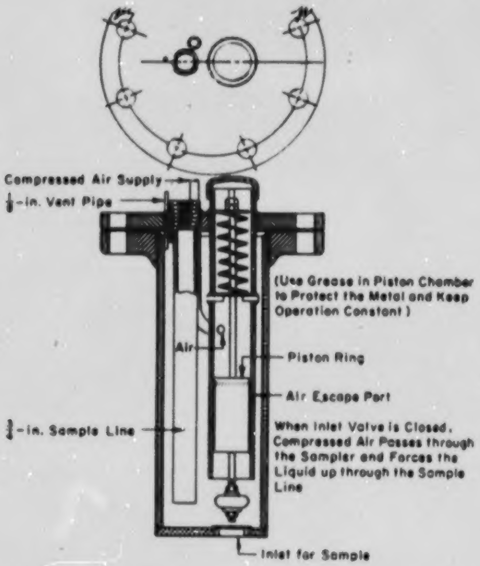
Compressed Air Supply
1/8-in. Vent Pipe
(Use Grease in Piston Chamber to Protect the Metal and Keep Operation Constant)
Air
Piston Ring
Air Escape Port
3/4-in. Sample Line
When Inlet Valve is Closed, Compressed Air Passes through the Sampler and Forces the Liquid up through the Sample Line
Inlet for Sample

Figure 19. Automatic sampler. This air-lift automatic sampler takes samples from a sewer when a pump cannot be used. (From Ref. 17, p. 124.)

Depth sampling requires special precautions to eliminate effects of pressure and temperature changes. Techniques of sampling waters under pressure, as well as surface waters, are described in detail in Refs. 17, Chapter VIII, and 4 (D-510-68). Fig. 21 illustrates an APHA type sampler used for sampling at moderate depths.

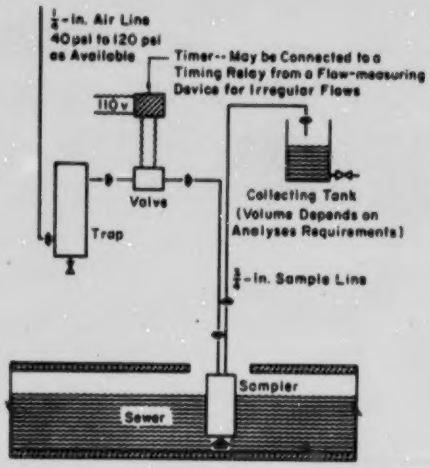
1/4-in. Air Line
40 psi to 120 psi as Available
Timer-- May be Connected to a Timing Relay from a Flow-measuring Device for Irregular Flows
110 v
Valve
Trap
Collecting Tank (Volume Depends on Analyses Requirements)
3/4-in. Sample Line
Sampler
Sewer

Figure 20. Schematic arrangement of automatic sampler shown in Fig. 20. (From Ref. 17, p. 125.)

Selection of a sampling site is determined primarily by two factors: a) the type of investigation, and b) the degree of mixing in the body of water to be analyzed. Rainwater and Thatcher (Ref. 62) recommend the use of a 3-dimensional grid intersection method of sampling, with samples taken at various depths as necessary to provide a representative sampling. If only a single sample is to be taken, it should derive from the center of the water mass.

Sampling frequency is determined by the variability of the source sampled. No important change in quality of the water should go unnoticed in an adequately planned sampling procedure. The U.S. Geological Survey follows the arbitrary rule for sampling once per day.

12.4.2 Sampling Apparatus: Materials and Handling

Sampling equipment is made from a variety of materials. Containers of hard rubber, polyethylene, and a few other plastics have been found satisfactory. No appreciable difference

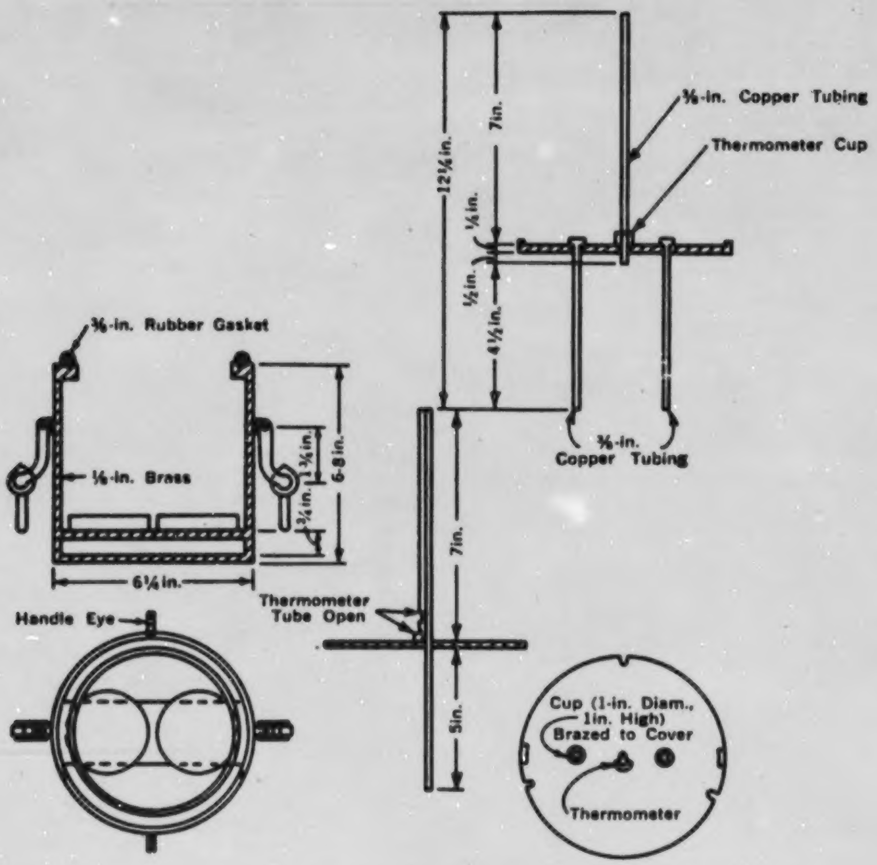
⅜-in. Copper Tubing
Thermometer Cup
12¼ in.
7in.
¼ in.
½ in.
4½ in.
⅜-in. Rubber Gasket
⅛-in. Brass
⅜ in.
6-8 in.
2¾ in.
6¼ in.
⅜-in. Copper Tubing
Handle Eye
Thermometer Tube Open
7in.
5in.
Cup (1-in. Diam., 1in. High) Brazed to Cover
Thermometer

Figure 21. DO and BOD sampler assembly. (From Ref. 7, p. 476.)

in the following characteristics was detected for pyrex vs. polyethylene containers: silica content, Na^+, alkalinity, Cl^-, boron, specific conductance or pH, when water samples were stored for about five months.

Soda lime glass sampling bottles are, of course, not recommended because of the risk of sample contamination through leaching of ions from the glass and/or ion exchange between the glass and the water sample.

The use of stainless steel tubing for sampling lines used in the acquisition of industrial water samples for DO testing is recommended by the ASTM Committee on Water (D-19). "The sample line shall contain a cooling coil (C.C.) if the water being sampled is above R.T., in which case, cool the water to 60-65°F (16-18°C). Where a C.C is used, the valve shall be at the inlet to the C.C. and the overflow shall be to a point of lower elevation." (Ref. 4, p. 93).

Standard BOD bottles have a capacity of 250-300 ml and are fitted with ground glass stoppers. They should be routinely cleaned with a good detergent and rinsed and drained thoroughly prior to use. The use of a water seal is recommended as a precaution against introducing air into the bottle during the incubation period. Inversion in a water bath of the BOD bottle containing the sample or the addition of water to the flared mouth of the (sealed) BOD bottle may be employed as the means of preventing air (O_2) diffusion into the sample.

Incubated samples should be placed in a thermostated bath at 20 ±1°C, and all light excluded during incubation to prevent additional oxygen production by algae.

12.4.3 Sample Preservation

For biochemically active samples it is best to analyze immediately after sampling. Where this is not possible the aliquot should be refrigerated at 4°C.

The matter of sampling precautions, volumes, and equipment is further discussed in ASTM Standards, Vol. 23 (Methods D-510 and D-596) and in this volume under H2O-DO, Section 2.1.

12.4.4 Procedures

ASTM procedures for the determination of dissolved oxygen in industrial wastewaters are described under methods D-888 and D-1589 (Ref. 4). For further discussion of reagents and procedures, pre-seeding of BOD samples, etc., see this chapter, Sec. 2.6 and Refs. 7, Sec. 219; 4, under methods D-888 and D-1589; see also Ref. 3, pp. 114-16. In addition, procedures are briefly discussed in this chapter under Sec. 7. See also this volume, chapter H2O-DO. Results are expressed in mg/l.

For a more detailed description of the standard method for reporting the results of water analyses the reader is referred to Refs. 4, D-596-69; and 17, p. 224.

13. BOD in Natural Waters: *In Situ* Environmental Factors

The development of OD below the point of discharge of an organic pollutant into a moving stream depends on a number of physical factors, of which stream geometry ranks as one of the most important (Refs. 63-64).

For a relatively deep body of water, the biological activity of soluble organic pollutants and/or those in colloidal suspension may be dispersed in a homogeneous manner. With the synthesis of microorganisms, some flocculation is likely to occur, followed by settling of flocculent in material and *anaerobic stabilization*. Under dynamic stream conditions, if the organic discharge is continuous, aerobic biosynthesis depends on the food/organism ratio. Thus, the stabilization rate for organics discharged to a stream is strongly dependent on whether or not a population of appropriate microorganisms is already present. If this is indeed the case, then a rapid increase in oxygen consumption and biosynthesis will occur.

In the case of a shallow stream, there is generally a favorable food/organism ratio. Because of the shallow depth, the area/volume ratio of bottom surface to stream is large. Generally shallow streams have relatively high velocities, providing turbulent flow conditions. These conditions favor rapid reaeration and microorganism growth. Just below the organic discharge, attached organisms may luxuriate. The stream here behaves as a *trickling filter* with a BOD removal rate considerably greater than for comparable pollution conditions in a deeper stream. The OD in the active zone (i.e., where attached organisms are feeding on the discharge) may be more closely correlated with BO than with BOD removal. Ultimately, the attached organisms may grow large enough to be detached by the stream current and be deposited down stream in a more quiescent section of the stream. In addition, *anaerobic stabilization* of settled materials will tend to reduce the oxygen consumption over that theoretically required to stabilize the organics and remove the initial BOD.

Resuspension of sediment during short periods of high stream velocity can have a profound effect on a column of water. It is well known that the short term BOD value of relatively stable organic matter of low (short term) BOD will be enhanced after a period of anaerobic decomposition in the stream sediment (Ref. 65). Resuspension of such sediments can suddenly impose an appreciable additional BOD burden on the stream. Jansa and Akerlindh (Ref. 66) studied the relationship between the amount of settleable solids found and the distance which the suspended solids were carried before settling out, as a function of stream velocity. They found that there is a sedimentation equilibrium point which exists downstream from a sewage outfall -- that is, a point where BOD deposition/day equals the amount oxidized/day. This is a reasonable assumption to make for those situations where only the oxidizable fraction of the suspension is a consideration, but may be applied with confidence only for those cases of stream pollution in which resuspension of the sediment is negligible. Under these (non-turbulent) conditions the following expression for oxygen depletion due to sedimentary BOD may be used to improve the fit of the Streeter Phelps (S-P) equation:*

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*The Streeter-Phelps equation takes the form: $dD/dt = K_1B-K_2D$, where D is the oxygen deficit at time t, B is the organic oxygen demand, and K_1 and K_2 are depletion and reaeration rate constants, respectively.

$$\frac{dI_s}{dt} = k_s L_s e^{-k_s t}, \text{ where} \qquad \text{(Eq. 26)}$$

I_s is settled sludge BOD at time t

L_s is the total quantity of settleable sludge BOD, and

k_s is the sedimentation rate constant.

This was found to be a useful relationship in describing the DO status of one sewage-polluted Swedish stream, where k_s was found to be 40 day^{-1}. It was further indicated by these workers that the settling of BOD-containing solids was negligible when stream velocities were >50 cm/sec.

Sludge-carrying capacity may be assumed to have a first-order dependence on stream velocity at low velocities, as a first approximation (Ref. 67). However, for stream velocities >12 cm/sec the capacity varies as the square of the velocity. The BOD of suspended solids may of course be experimentally determined. Similarly, their settleability under simulated flow conditions or at $v = 0$ is empirically verifiable. However, the trend toward adequate settling of BOD solids should render the sedimentation term of the S-P expression superfluous and merely a matter of academic interest in the treatment plants of the future.

For the description of a general design model for sedimentation basins showing the effects of such parameters as geometry, flow velocity, and particle size, density and quality, see Refs. 68a to 68c inclusive.

It should be noted that "physiologically inert"* brines such as NaCl or Na_2SO_4 may, by virtue of competition of their anions with phosphate for sorption sites, favor the release of $PO_4^{\equiv}$ from sediment, and thereby promote eutrophication. For this reason increase in the ionic strength of a site due to the desorption of salts may be expected to increase the eutrophication rate.

14. Some BOD-Related Phenomena in Natural Waters

There are two principal aspects of biological processes: one involves the *self-purification* activity of plants and animals which transforms potentially harmful substances into innocuous metabolic products, generally forfeiting DO in the process and frequently utilizing some of the species normally present in the unpolluted waters.

The second aspect involves biotal changes in response to pollutants. Thus biota may be used as quality criteria and as means of assessing environmental impact of pollution. For comprehensive treatments of the biological aspects of wastewater management see Refs. 69a, b, c, d, and e. The latter reference (69e) is a collection of classical papers, including the pioneering contributions of Kolkwitz and Marsson (Refs. 70a and b).

14.1 Self-purification

Self-purification, as the name implies, is the process whereby a stream rids itself of pollutants (impurities). Waste materials introduced into a body of water affect the biota directly and indirectly. The effect of waste may be lethal, or it may be more subtle, affecting behavior of biota, or reproduction, adversely.

The toxicity of substances or mixed wastes is determined by means of bioassays using fish, larvae and other invertebrates or microbes. A variety of laboratory procedures are used, but the methods of Doudoroff et al have become standard (Ref. 71). See also Standard Methods, 13th edition. For toxicity and bioassay methods, see Chapters 13 and 14 of Ref. 39, Vol. 2 (Refs. 72a and b).

14.2 pH and BOD

Photosynthetic and respiratory activities of biota have a direct effect on the CO_2 content of streams, and the diurnal variation in pH as a result of these processes is usually of the order of ±0.5 pH unit. However, in the presence of intense algal growth, it is possible for the pH to approach the upper physiological limit by the end of the day. This may be illustrated by the simplified equation below which considers only the calcium bicarbonate in fresh waters:

$$\begin{array}{ccc} Ca(HCO_3)_2 - 2CO_2 & \text{(photosynthesis)}\rightarrow & Ca(OH)_2 \\ \downarrow & & \downarrow \\ \ulcorner Ca^{++} + 2(HCO_3^-)\urcorner & & \ulcorner Ca^{++} + 2(OH)^- \urcorner \end{array} \qquad \text{(Eq. 27)}$$

This reaction clearly favors increase in pH. The relationship of the various carbonic chemical species of the pH range 4-10 is shown in Table 12. However, in soils (particularly when water-logged), and in deep waters of lakes, the total content of carbonic species may go far beyond the level implied by solubility equilibria due to anaerobic metabolic processes (Benoit, *Op. cit.*, Ref. 67).

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*The term "physiologically inert" is here used in the eutrophication sense only.

Table 12

Dependence of Carbon Dioxide, Bicarbonate, and Carbonate Ratios on pH Values[a]

pH	CO_2	HCO_3^-	$CO_3^{=}$
4	0.996	0.004	$\sim 10^{-9}$
7	0.21	0.79	$\sim 10^{-4}$
9	0.003	0.966	0.03
10	10^{-4}	0.76	0.24

[a] *Adapted from Ref. 73.*

14.3 Organic Matter

Natural waters contain organic matter in the form of living animals and plants, their nonliving particulate remains (*detritus*) as well as their soluble organic residues and excretions. It has been estimated by Parsons (Ref. 74) that the surface waters of the North Atlantic contain approximately 2 mg/l of soluble organic matter, 0.2 detritus, 0.04 phytoplankton, 0.004 zooplankton and 0.00004 fish. Fresh waters contain perhaps 10 times as much organic material. The differences are related to the more direct organic contribution which fresh waters receive from the land rather than to any great difference in productivity.

14.4 Dissolved Oxygen Relations

Dissolved oxygen (DO) is a very commonly used water quality criterion (see this volume, H2O-BIO, DO). Loucks (Ref. 75) and coworkers give the following description of DO relations in a stream polluted with oxygen-consuming waters:

$$\frac{dB}{dt} = (K_1 + K_3)B + R, \text{ where} \qquad \text{(Eq. 28)}$$

$\frac{dB}{dt}$ is the rate of change of BOD with time,

B is the BOD present at time t, and

R is the rate of BOD addition from runoff and scour.

K_1 and K_3 are rate constants for deoxygenation and sedimentation, respectively.

A related expression in terms of the DO deficit, D, is:

$$\frac{dD}{dt} = K_1B - k_2D - A, \text{ where} \qquad \text{(Eq. 29)}$$

$\frac{dD}{dt}$ is the change in DO deficit with time,

D is the difference between existing [DO] at time t and the saturation value,

A is the net rate of oxygen production from the photosynthesis-respiration cycle, and

K_2 is the reaeration rate constant.

Integration of equations 28 and 29 above results in:

$$B_t = (B_o - \frac{R}{K_1 - K_3})e^{-(k_1 + k_3)t} + \frac{R}{K_1 + K_3}, \qquad \text{(Eq. 30)}$$

and

$$D_t = \frac{K}{K_2 - K_1 - K_3}\left[(B_o - \frac{R}{K_1 + K_3})e^{-(K_1 + K_2)t} - e^{K_2 t}\right]$$

$$+ \frac{K_1}{K_2}\left[(\frac{R}{K_2 + K_3} - \frac{A}{K_1})(1 - e^{-K_2 t})\right] + D_o\, e^{-K_2 t} \qquad \text{(Eq. 31)}$$

In Table 13 the reaeration coefficient K_2 was calculated from experimental data obtained under actual stream conditions. Typical values of the parameters involved are shown in columns 2 through 6; of K_1 (the deoxygenation coefficient), in column 7.

The data for K_2 are summarized in Table 14 on page 31 (Ref. 14).

Equation 30 is that of a typical oxygen sag curve (Fig. 22). The minimum t_c in the figure reflects the time of minimum DO value. Prior to t_c, reaeration dominates. From velocity information for a stream one can determine the location of the critical point. The oxygen sag equation is applicable only on the assumption that K's, A and R all remain essentially constant throughout the time element for which the calculation is made and that values for these constants are either obtainable or may be reasonably estimated. For (A, K_3, R) = 0, equation 31 reduces the classic equation of Streeter and Phelps (Ref. 14).

The minimum cost of meeting any given set of DO standards for the river reaches of a basic system may be determined using the model of Loucks and coworkers (Ref. 75).

14.5 Temperature

While temperature is not included as a variable in the DO model, it certainly has a profound effect on oxygen solubility, reaeration, sedimentation and animal and microbial functions (see also this volume, H2O-BIO: DO, Sec. 1.2). Bradshaw and Davidson (Ref. 76) discuss both negative and positive effects of increased temperature on pollution and develop

Table 13

Factors in resultant oxygen formula (1) obtained from data in Table No. 1, Ref. 14, P. 18*

Notation:

D_A = Observed dissolved oxygen content of the river at the upper station, in terms of parts per million of deficit below the oxygen saturation value at the mean river water temperature between the two stations.

D_B = Observed dissolved oxygen content of the river at the lower station, in the same terms as (D_A).

L_a = Corrected initial oxygen demand at the upper station, in terms of parts per million of oxygen.

t = Mean time of flow from the upper to the lower station, in days.

T = Observed mean temperature of the river water, in degrees Centigrade.

K_1 = Coefficient of deoxygenation at the observed mean river water temperature. (Calculated from a value, 0.1 at 20° C.)

K_2 = Coefficient of reaeration, calculated from the other terms.

Month	At temperature of river water							K_2 (at 20° C.)	Mean velocity of flow (feet per second)
	D_A (parts per million)	D_B (parts per million)	L_a (parts per million)	t (days)	T (° C.)	K_1	K_2		
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
Station 3 to station 11:									
May 1914	0.89	0.63	2.54	0.21	15.9	0.083	0.990	1.38	2.48
June	3.13	1.09	1.91	1.07	24.5	.123	.544	.35	.50
July	4.00	1.32	2.73	1.81	24.6	.124	.380	.25	.29
August	5.53	1.95	4.22	2.73	24.8	.125	.276	.17	.19
September	6.28	2.49	3.59	3.06	20.8	.104	.197	.18	.18
Oct. 1-15	8.63	3.11	3.30	6.23	18.7	.094	.105	.12	.09
Station 11 to station 19:									
May, 1914	.63	.72	4.89	.18	15.9	.083	.245	.34	2.50
June	1.09	1.14	2.20	.77	24.5	.123	.192	.12	.59
July	1.32	1.04	2.54	1.36	24.1	.121	.289	.20	.32
August	1.95	1.60	3.44	1.98	24.4	.122	.217	.14	.22
September	2.49	1.09	3.14	2.30	20.5	.102	.144	.14	.19
Oct. 1-15	3.11	2.60	1.74	4.37	18.6	.092	.052	.06	.10
Station 23 to station 65:									
May, 1914	.85	1.22	5.16	.62	16.3	.084	.200	.30	4.20
June	1.33	.93	2.94	1.90	22.9	.115	.330	.25	1.36
July	1.24	.94	2.65	3.00	24.8	.124	.230	.15	.86
August	1.88	.75	3.69	4.90	24.4	.121	.260	.17	.63
September	3.77	.76	2.56	6.14	20.0	.100	.190	.19	.43
Oct. 1-15	2.83	.50	15.74	11.35	18.0	.091	.353	.43	.23
Station 65 to station 77:									
May, 1914	1.22	.72	4.89	.18	15.9	.083	.245	1.11	3.64
June	.93	.46	3.08	1.02	23.2	.116	.801	.59	.71
July	.94	.54	2.14	1.73	24.8	.125	.436	.28	.44
August	.75	.49	1.26	2.47	24.4	.122	.253	.17	.31
September	.76	.44	1.92	2.54	20.0	.100	.334	.33	.31
Oct. 1-15	.80	.80	3.34	5.02	18.0	.091	.189	.23	.15

*Integrated form of the S-P equation, see footnote, p. 28)

Table 14

Derived values of (K_2) at 20° C. (from Table No. 13)
(from Ref. 14, p. 38)

Stretch	May (1914)	June	July	August	September	Oct. 1-15	October	November	December	January (1915)	February	March	April
3-11	1.38	0.35	0.25	0.17	0.18	0.12	......	......	......	......	......	......	......
11-19	.34	.12	.20	.14	.14	.06	......	......	......	......	......	......	......
23-65	.30	.25	.15	.17	.19	.43	......	......	......	......	......	......	......
65-77	1.11	.59	.28	.17	.33	.23	......	......	......	......	......	......	......
77-88	1.07	.71	.33	.16	.70	.16	......	......	......	......	......	......	......
104-349	.24	.18	.12	.14	.15	.22	......	......	......	......	......	......	......
349-461	.16	.65	.28	.15	.13	.33	......	......	......	......	......	......	......
475-482	.29	.32	.33	.26	.40	......	0.73	3.98	0.96	1.14	0.61	1.43	1.09
482-488	.05	......	.13	.07	.05	......	.35	.81	.39	.10	.78	.71	.14
492-598	.27	.32	.57	.46	.61	......	.31	......	1.05	.99	.59	.65	1.88
598-611	.21	.36	.47	.43	.87	......	.54	......	.75	.58	2.44	.82	......

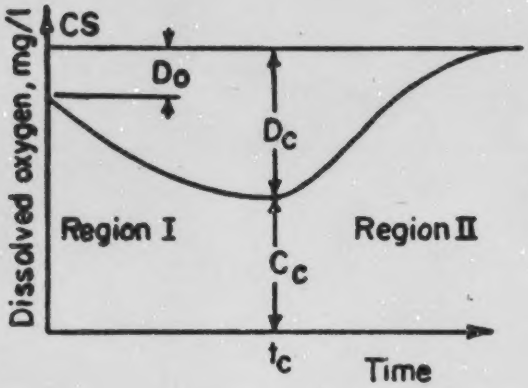

Figure 22. Oxygen sag curve. C is dissolved oxygen (DO) saturation; D_o is initial DO deficit; D_c is critical DO deficit; C_c is critical DO level (from Ref. 75).

a mathematical expression for the temperature effect on the DO of streams carrying a BOD load. Their mathematical model indicates that, theoretically, at least, there exists an optimum temperature profile at a location downstream from a (BOD) pollution point source. This is illustrated with specific examples studied by the authors.

14.6 The BOD Plateau

In two papers (Refs. 77 and 78) Torpey has given valuable empirical data which help evaluate mathematical models. He examined the pattern of the long-term summer DO levels vis à vis BOD loads. Such studies should be most helpful in the planning of long range programs for the monitoring of water quality. Torpey's data are interpreted as evidence for the existence of a "homeostatic"* DO plateau (Fig. 23) in the range of 30% to 50% oxygen saturation. BOD loading rates ranged between 20-135 lb/day/acre in these estuaries with depths which averaged ∿30 ft. Oxidation to NO_3^- of the nitrogenous materials present was not evident during the plateauing, and Torpey interpreted the plateau phenomenon as resulting from symbiosis between the algae present which provided photosynthetic oxygen and bacteria which synthesized essential mineral nutrients for the algae.

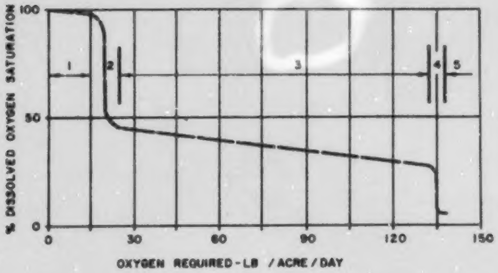

Figure 23. Response of New York Harbor and Thames Estuary. (Ref. 78)

14.6.1 The BOD Plateau and Zoning

Torpey divided the plot into three *ecological zones*, the first of which supported biota such as mollusks, crustacea, and fish (higher forms in the food chain). The "homeostatic plateau" (zone 3) has a primarily microbial biotal composition. He concluded that for loading rates exceeding the plateau region of oxygen requirements, the introduction of sewage treatment by no means guarantees the DO content will undergo any marked increase. For such systems as the Thames and New York harbor, oxygen sag considerations alone will not be indicative of the degree of treatment required for these waters to be restored to a condition enabling them to support large fish populations. To achieve this goal generally demands much more intensive treatment than implied by these indications.

Stream sediments make an important contribution to *total oxygen demand (TOD)*. Oldaker, Burgum and Pahren (Ref. 79) studied the OD of both aged and young river sediments related to sewage outfall. The effects of sediment depths on OD under quiescent conditions were examined in 20 liter carboys. Coincidentally, information was obtained as to the burden incurred where a system is subjected to severe scouring conditions, such as the resuspension of solids during a period of turbulent flow. In-field conditions which normally obtain (i.e., where benthic animals disturb the bottom muds somewhat) are usually intermediate between the extremes of complete quiescence and total resuspension.

Fair and coworkers (Ref. 80) had earlier observed that it took more than a year for attainment of the ultimate OD by bottom muds.

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*Homeostasis - Homeo (same); statis (condition)
Homeostatic Plateau - relative OD equilibrium exists in this range.

14.7 Reaeration

The absorption rate of oxygen in natural waters is given by the following equation:

$dc/dt - k_2 (C_S - C)$, where (Eq. 32)

C is the measured [DO],

C_S is the saturation value at the temperature of dissolution, and

k_2 is the coefficient of aeration.

Durum and Langbein (Ref. 81) demonstrated the effects on the aeration coefficient of velocity, v, and depth, H (hydraulic effects). In their study of the Kansas-Mississippi-Missouri River system they demonstrated that k_2 decreases as the square root of the mean discharge rate in the downstream direction. This is in the same direction as the variation in stream height and velocity with discharge (depth increases as the 0.4 power, velocity as the 0.1 power of discharge). These same workers also demonstrated regional differences in the square root relationship, k_2 varying as $15 \sqrt{Q}$ for coastal plain rivers, and as $80 \sqrt{Q}$ in the (northern) Rocky Mountain region, where Q is the mean discharge rate in cubic feet per second. This difference has been related to the slopes of the respective stream beds, since the regions represented are extremes with regard to slope.

There is a general downward trend in reaeration coefficient with increasing height or 'stage' of a river, but shallow reaches *(riffles)* behave differently from deeps or pools. Fig. 25 illustrates a rapid decrease in k_2 with increase in discharge rate; conversely, for pools k_2 increases (more moderately) with increase in discharge. Ultimately the distinction between these stream features disappears at some high stage.

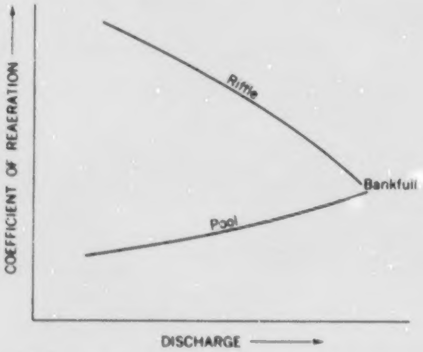

Figure 24. Effect of discharge on aeration (from Ref. 81, p. 4).

Langbein and Durum also estimated nationally the total assimilation capacities for a variety of streams in eight size categories. With their data it is possible to estimate the BOD capacity in tons of oxygen-consuming substances which can be assimilated/mile under conditions which would reduce DO (in mg/1) by one unit. Table 15 lists the assimilatory capacities for three classes of stream: small (I); medium (II); and large (III).

Table 15

Relation of Assimilatory Capacity and Stream Size[a]

Stream class	Assimilatory capacity[b]	Average depth, ft	Assimilatory capacity per ft of depth	k_2 day^{-1}
I	0.04	0.55	0.07	9.5
II	1.0	5.0	0.2	—
III	5.2	45.0	0.12	0.1

[a] *From Ref. 84.*

[b] *Tons of BOD per mile per unit O_2 deficiency.*

15. Waste Assimilation

There are two classes of biological processes which predominate in waste assimilation. They are (1) the photosynthetic and respiratory processes of plants and (2) the ingestive (feeding), digestive and respiratory processes of animals. The latter group includes microscopic multicellular animals and protozoans; the former includes microscopic algae, bacteria and fungi. Although bacteria and fungi can absorb organic matter from solution and digest the absorbed materials, they are commonly found adsorbed onto the surfaces of organic particulate matter. In this case extracellular enzymes are believed to function as mediators in the feeding cycles of the bacteria and fungi. They are, furthermore, known to thrive under conditions unfavorable to the higher plant and animal species, and are therefore the dominating biotal population where stream pollution is most severe.

Bacteria and microalgae constitute the chief food of most protozoan species. In addition they constitute an important food source of the so-called filter-feeding (micro- and macroscopic) invertebrate species. The Chinese adage which may be translated as "big fish eat little fish; little fish eat shrimp, and shrimp eat mud" is a succinct description of the food chain (or web) concept. However, the significance of the "mud" in question is overlooked in the ancient adage. It is, in fact, at the base of the food chain, consisting of the partially decomposed remains of plants and animals, and/or the products of the photosynthetic cycle.

Stream oxygenation is effected by two (often simultaneous) processes: (1) the diffusion of atmospheric O_2 in the water and (2) the provision of a net excess of oxygen in the photosynthetic cycle:

$$\begin{aligned} CO_2 + H_2O \xrightleftharpoons[\text{respiration}]{\text{photosynthesis}} CH_2O &+ O_2 \\ \hookrightarrow (CH_2O)x & \end{aligned} \qquad \text{(Eq. 33)}$$

The photosynthetic component may be further identified according to sources of the contribution as benthic flora -- *epiphyton*, *periphyton* and/or the free floating microscopic plant species known as *phytoplankton*.

Theoretically, the net O_2 production in the cycle represented by Equation 33 above is zero. The formaldehyde polymer $(CH_2O)x$ of the equation schematically represents the carbohydrate production in plant photosynthesis. However, proteins and fats are also synthesized. For nitrogenous compounds such as the proteins or nucleic acids, a source of nitrogen is clearly required, as well as sources of sulfur and phosphorus.

The energy required is supplied by the carbohydrate respiration in the photosynthetic process. Thus, one would not expect a positive net yield of oxygen where anabolic activity is high. However, the removal of plant matter downstream from the active water zone, or the settling of plant tissue to the stream bottom where decomposition may either stop or proceed by an anaerobic mechanism, disturbs the equilibrium situation represented in Equation 33 and results in available oxygen at the water zone in question.

Oxygenation components in streams were measured directly by Stay and coworkers (Ref. 83). These included such parameters as diffusion rates, the photosynthesis of periphyton and phytoplankton, and respiration. The standard practice of using light and dark bottles (Ref. 7, Sec. 601 E)* to exclude or permit photosynthesis, has a number of serious disadvantages: a) it obviates the important contribution of benthos in shallow streams;
b) since bottle conditions are stagnant they do not reflect the normal states of interchange between nutrients and the wastes produced in streams; and c) the ratios of surface-to-volume which obtain are excessively high and do not reflect natural conditions, either.

In order to reflect more accurately stream conditions in their field studies, Stay and coworkers used three types of large plastic chambers; the first was sealed to the atmosphere and transparent; the second, also sealed but opaque; and the third chamber was both open and transparent. The chambers were designed for use with either artificial or natural substrates and natural flow velocities were simulated by paddle wheels which were driven either by artificial means or by the use of external water-wheels. Sampling and analysis for gases in the vapor phase as well as those in aqueous solution (i.e., O_2, CO_2, etc.) were possible. The Type 1 chamber (i.e., sealed but transparent) permitted photosynthesis and respiration to go on as simultaneous events or processes, but the atmospheric exchange or diffusion of CO_2 or O_2

Table 16

Component Processes in Stream Metabolism from Chamber-Dissolved Gas Measurements

Chamber type	Configuration	Process occurring	Change in dissolved gases
1	Transparent, closed to atmosphere	Photosynthesis, respiration	$O_2\uparrow : CO_2\downarrow$ $O_2\downarrow : CO_2\uparrow$
2	Opaque, closed to atmosphere	Respiration	$O_2\downarrow : CO_2\uparrow$
3	Transparent, open to atmosphere	Photosynthesis, respiration, diffusion	$O_2\uparrow : CO_2\downarrow$ $O_2\downarrow : CO_2\uparrow$ $O_2\updownarrow : CO_2\updownarrow$

(Ref. 83)

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*For a detailed description of biological sampling and analysis, see Ref. 7, Sec. 600 ff.

was not possible. Chambers of Type 2 (opaque) permitted only respiration. Only in Type 3 -- the open, transparent chamber -- do all three processes (i.e., respiration, photosynthesis and diffusion) occur. Thus, it was possible to measure net photosynthesis (i.e., excess of photosynthesis over respiration) using a Type 1 chamber. Similarly the sum of data from Types 1 and 2 chambers is a measure of the gross photosynthetic process. Subtraction of Type 3 data from Type 1 yields the gas exchange between air and water, etc. The processes involved are enumerated in Table 16. Contributions of benthos vs. phytoplankton were measurable by simply damming off the upper chamber substrates. The predominant effects of the former (benthos) was thus clearly shown by these workers in their studies of the Blue River (Oklahoma). The photosynthetic effects of diurnal variations in light intensity were also apparent.

Gaseous exchange phenomena in river ecosystems represent one of a large number of biotal processes occurring in streams. It is not possible to measure dynamic relationships between biota by the relatively simple physiochemical techniques available for the measurement of non-living variables (trace metals, for example). It therefore becomes essential to provide as complete a description of biota as feasible, subsequently providing a suitable theoretical model of the ecodynamics involved in the system.

16. Bio-oxidation Processes in Waste Treatment

Biological waste treatment systems are generally recognized as the most efficient means of removing organics from wastewaters. A discussion of these systems is outside the scope of this chapter, and the reader is referred to Genetelli's excellent description of the three basic systems most often employed in waste removal: a) *activated sludge* (AS), b) *trickling filters* (TF), and c) *aerobic oxidation* (AerOx) lagoons (Ref. 84).

Treatment units for organic wastes may 1) convert the waste to CO_2 and other decomposition products or 2) convert the organics to some settleable form. While the system characteristics may differ as to, say, oxygen requirements, the manner in which biological slimes are utilized, or the waste detention time required to complete treatment, the basic biochemical processes involved are alike.

The production of CO_2, water, and NH_3 during an aerobic waste treatment process is, of course, oxygen-dependent. The energy liberated from the H-transfer process is both consumed in the cellular synthesis and utilized by the cellular products to fulfill their energy needs. The quantity of O_2 required to oxidize the organic pollutants will depend largely on *biological oxygen demand (BOD)** satisfied during the biological treatment process (Ref. 84 above). Treatment methods vary somewhat in the percentage capability of satisfying applied BOD, with the converted activated sludge method ranking first (90-95%), low rate trickling filters in second place (80-90%), and high rate trickling filters third (65-85%) (Ref. 85).

The disappearance of organic material during bio-oxidation results in new cell synthesis. The amount of new cellular material produced per pound of BOD load is a function of the chemical composition of the substrate (Ref. 86). Helmers and coworkers reported that solids production varied with BOD removal and Okun (Ref. 87) also found that the total

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*Normally BOD is the notation for *biochemical oxygen demand.*

Table 17

Division of Substrate between Oxidation and Synthesis[a]

Class of compound	Per cent		
	Range present	Oxidized mean	Converted to sludge
Carbohydrates	5-25	13	65-85
Alcohols	25-38	30	52-66
Amino Acids	22-58	42	32-68
Organic acids	30-80	50	10-60

[a] 24-hr, batch-fed activated sludge system. Units lbs/1000 $ft.^3$ (from Ref. 88)

quantity of new cell materials formed was a function of BOD loading. With high load ratios high growth rates were obtained, whereas low loadings resulted in sludge destruction. Table 17 shows the influence of substrate type on the proportion of oxidation and synthesis obtained in 24-hour, batch-fed AS systems (Ref. 88). The variation in conversion yields may be rationalized on the basis of different utilization rates or efficiencies for different substrates given a specific set of organisms.

16.1 BOD-Related Parameters

The "nutrient substrate" or food value of wastewater is defined in terms of *BOD (biochemical oxygen demand)* of the constituents present. So-called "Loading Parameters" have been variously defined (Ref. 84, pp. 420-26), but invariably relate to the efficiency of BOD removal from a substrate. However, since BOD removal efficiencies of the order of 90% may be achieved for loadings ranging from 30 to 120 lb/1000 ft^3, it is clear that such relationships are of little value. Similarly, parameters based on the volume of treatment tanks fail to consider the solids aerated or the aeration time. These considerations led the Water Pollution Control Federation to recommend that *sludge loading ratio (SLR)* be used as the loading parameter for AS systems. This parameter is expressed in terms of lbs BOD/day/lb MLVSS and thus reflects the ratio of food to organisms. This parameter (SLR) is synonymous with the symbol F often encountered in mathematical formulations used to describe waste treatment systems.

Another, more recently suggested parameter utilizes lbs of BOD/day/unit weight of *deoxyribonucleic acid (DNA)*. As a reflection of cell material available in the system, DNA would appear to offer a reasonably accurate means of determining the food/organisms ratio (Ref. 90). The DNA parameter has proved the one most useful in predicting specific operational upsets (Ref. 91).

16.2 Bio-oxidation Summary and Conclusions

Technology is presently available for effecting up to 95% removal of organics (BOD) in waste waters. Conventional waste water treatment is capable of removing only about 25% of the total solids which may be present in domestic waters (more than 750 mg/l). In recent years the excessive enrichment (eutrophication) of receiving waters by nutrient-rich wastes has also emerged as a major problem for which conventional treatment methods are inadequate. These difficulties along with our diminishing supply of potable waters have led to a more intensive examination of the area of advanced waste treatment (AWT) methods (Ref. 84).

Advanced waste treatment requires a) the concentration and disposal of impurities present in municipal waste waters and b) the establishment of markets for the relatively pure waters which can be produced by such advanced treatment systems. An inherent requirement of these advanced systems is the concomitant development of effective methods of disposal of recovered concentrated pollutants so that they will not re-enter the water cycle. Thus, water *pollution* and *supply* problems may both be solved simultaneously by the development of advanced treatment systems.

17. BOD: Future Trends

In 1971 the BOD Task Group of Committee D-19 in Water (ASTM) withdrew the 5-day BOD test (BOD_5) D2329-68 for industrial and industrial waste waters. At the time this decision was made it was hotly contested and it remains a highly controversial one today. The reasons for the Committee's decision to discontinue BOD_5 as an ASTM standard procedure are evident from a consideration of the limitations of the method as discussed under Sec. 4, and under Sec. 11 we have attempted to explore some viable alternatives to the standard BOD_5 procedure which would have the advantages of greater reproducibility and shorter analysis times (1-8 hours) whilst still utilizing those features of bio-oxidation which are uniquely suited to dealing with municipal wastewater analysis.

The use of the mass culture aeration analytical technique coupled with the ΔCOD concept (Sec. 11.3.2) appears to offer considerable promise. The concept of energy oxygen, determined by means of the Warburg Respirometer which measures O_2 uptake (p. 20), offers yet another promising alternative. Differential oxygen uptake has also been measured by an oxygen probe in one STOD procedure (Ref. 44).

The use of BOD-COD or BOD-TOC ratios has gained favor in recent years (see Sec. 3). Often BOD_5 is used in conjunction with a more rapid chemical method, since it is quite possible to correlate the two for a particular kind of waste. Thus, the best features of both methods are utilized -- BOD giving the longer term picture, with a rapid COD method furnishing the necessary short-term interim information.

Finally, the BOD_5 test has a long and respectible tradition of useful application behind it, is presently still in wide use in certain industrial and essentially all sewage treatment plants -- and particularly in the latter instance -- will probably survive in its present form for some time to come.

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INTRODUCTION

The ecosystems of natural streams, as well as systems such as municipal sewage facilities, are essentially biological reducing agents, and the *Biochemical Oxygen Demand (BOD)* test which has been so extensively employed in their monitoring is based on the biochemical oxygen requirements of these systems. Because of the inherent difficulties of the 5-day BOD test discussed in the BOD Section 4 of this volume, (length of time required for analysis, seed variability, and the need for acclimatization, toxicity, etc.) chemical methods have been developed. Although extreme care must be exercised in correlating BOD with *Chemical Oxygen Demand (COD)*, the potential for automation of the latter measurement and its relative rapidity and reliability have recently catapulted it into favor (Ref. 1).

1. Historical

The removal of organic matter from effluents usually involves oxidative processes, particularly in secondary treatment. Although there has been extensive quantitative investigation of the amount of oxygen necessary for the removal of a variety of organics, no universal procedure has been found to cover the wide variety of effluents analyzed (Ref. 2). Of the many methods suggested over a span of more than 100 years*, only three have gained prominence. Two of these are chemical, the third involving a biochemical procedure (see this volume, H2O-BOD).

The two chemical methods are: (1) oxidation by boiling acid potassium dichromate (i.e., the *dichromate value*) and (2) the *permanganate value* (no longer used in the United States) obtained by oxidation of the effluent with acid potassium permanganate ($KMnO_4$). Both methods will be described in greater detail in later sections. However, the salient points related to their applicability and limitations will be discussed below. Both methods determine an oxygen equivalent value, oxygen playing no direct role in the oxidations.

1.1 Dichromate Value

Adeney and Dawson (Ref. 4) introduced the use of potassium dichromate ($K_2Cr_2O_7$) in boiling acid solution in the determination of *oxygen absorbed (OA)* by effluents. This procedure in modified form has since come to be known as *chemical oxygen demand* or *COD* in the United States. A more detailed description of the method is given in section 5ff of this chapter and in the 13th edition of Standard Methods (Ref. 5). As is the case in the permanganate procedure, only a portion of the organic matter (depending on structure) is oxidized by the dichromate, and nitrogenous organics generally resist oxidation by this reagent. The method does not differentiate between biochemically stable and/or unstable organics. Thus, COD does not normally correlate strictly with the BOD of the effluent. Nonetheless the (silver sulfate-catalyzed) dichromate oxidation method is generally preferred over the acid $KMnO_4$ oxidation because of its greater reproducibility and wider applicability (Ref. 2).

1.2 Permanganate Value

The determination of oxygen equivalent from acid permanganate solutions is the oldest of the oxygen demand tests now in use, deriving its great popularity from its simplicity and rapidity. Since this is one of the earliest procedures used to assess pollution, the permanganate oxidation method provides a continuing basis for comparison with data obtained in prior determinations. Usually this method is a feasible one for use in routine control analyses. It has also been used where toxicity precludes the use of the 5-day BOD analysis.

The *permanganate oxygen consumed test*, as it was originally (and incorrectly) termed, has serious disadvantages. It is not always effective as an oxidant for many of the organic compounds found in sewage and particularly in industrial waste. Secondly, results depend strongly on both the size of the sample and the strength of $KMnO_4$ used. This latter problem was circumvented in part by adjusting the amount of permanganate so that not less than 25% of the reagent -- and no more than 50% -- was consumed at the end of the test. The method is both time- and temperature-sensitive. Time was standardized to 1/2 hour, and fluctuations in temperature over the period influenced the reproducibility of the results obtained. Moore (Ref. 18) compared four tests with the standard permanganate procedure (Ref. 6). Three of the tests used potassium dichromate, the fourth, iodic acid as the oxidizing agent. The iodic acid procedure is long and rather complicated, but the reagent has excellent oxidizing power and the test has good reproducibility.

In Great Britain the permanganate value is usually determined at 3 minutes and 4 hours (Ref. 7). The 3-minute test measures immediate oxygen demand of the sample from both inorganic and any *easily oxidizable* organic sources. The presence of ferrous salts, nitrites, phenols, sulfites, sulfides, thiocyanates and/or thiosulfates results in high 3-minute permanganate values.

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*For further historical references see the end of this chapter, including Ref. 2 and Moore, Kroner and Ruchhoft (Ref. 3).

When the 3-minute permanganate value is low, the 4-hr value provides a relatively rapid and simple method of measuring total oxidizable organic (and inorganic) constituents of sewage and plant effluents as well as river waters. Here (i.e., when the 3-minute $KMnO_4$ test yields a low value) a high 4-hr value generally indicates pollution.

The ratio: 4 hr:3 min permanganate value can be significant, frequently providing a clue as to the cause of the pollution. Thus, effluents from domestic sewage sources, rivers, etc., containing untreated sewage normally yield a ratio of ~ 3. However, certain industrial wastes disturb this ratio, gas liquor tending to lower the value to ca. 2. On the other hand, waters polluted with vegetable wastes usually have a high 4 hr:3 min ratio which may lie between 4-10. This is illustrated in Tables 1, 2, and 3.

Table 1
Ratio 4 h:3 min permanganate value for a final effluent from domestic sewage (Bolton, Longworth) (Ref. 7, p. 121).

Date	*Permanganate value* p.p.m.		*Ratio* 4 h:3 min
	3 min	4 h	
2.2.49	2·8	8·6	3·1
11.1.50	3·6	10·2	2·8
3.12.50	1·4	4·2	3·0
30.5.51	2·6	7·6	2·9
10.10.51	4·0	10·8	2·7
5.2.52	1·6	5·6	3·5
24.6.52	2·0	6·8	3·4
3.2.53	2·4	7·2	3·0
13.5.53	3·2	9·6	3·0
3.9.53	2·4	7·2	3·0
		Average –	3·0

Table 1 shows typical 4 hr:3 min ratio of ca. 3 for a domestic sewage source; table 2, the ratio for a sewage effluent carrying about 20% by volume of gas liquors. In the last table, a comparison of the 4 hr:3 min ratios above and below a gasworks discharge shows the marked effect of the effluent on this value.

As with the dichromate oxidation, the permanganate method is used as an empirical measure of chemically oxidizable matter, and nitrogen compounds are similarly resistant to oxidation.

Table 2
Ratio 4 h:3 min permanganate value for a final effluent from sewage containing about 2 per cent by volume of gas liquor (Ref. 7, p. 121).

Date	*Permanganate value* p.p.m.		*Ratio* 4 h:3 min
	3 min	4 h	
6.8.47	20·8	42·2	2·0
16.12.47	25·4	54·0	2·1
11.2.48	20·4	44·4	2·1
24.6.48	12·4	27·6	2·2
28.4.49	25·2	51·4	2·0
13.10.49	15·6	31·8	2·0
18.5.50	30·8	62·8	2·0
19.10.50	14·0	30·8	2·2
18.4.51	19·0	42·6	2·2
9.1.52	13·2	29·6	2·2
		Average –	2·1

Table 3
Ratio 4 h:3 min permanganate value for rivers above and below gasworks discharges of gas liquor (Ref. 7, p. 122).

River		*Date*	*Permanganate value* p.p.m.		*Ratio* 4 h:3 min
			3 min	4 h	
R. Douglas	above gasworks discharge .	3.7.53	6·0	18·0	3·0
	below gasworks discharge .	3.7.53	59·8	93·0	1·6
R. Irwell	above gasworks discharge .	6.5.53	3·6	12·0	3·3
	below gasworks discharge .	6.5.53	19·0	40·0	2·1
R. Medlock	above gasworks discharge .	15.4.53	1·6	5·2	3·3
	below gasworks discharge .	15.4.53	320	530	1·7

Thus, the scope of this analysis is limited and results obtained from it have only a rather ill-defined relevance to the ultimate chemical or biochemical OD of a system, depending on the chemical nature of the constituents present in the system. Because of this limitation, instructions in the use of the permanganate method generally stress the importance of rigorous adherence to specified conditions if valid comparisons are to be made.

Of the extensive research carried out on variants of the permanganate oxidation, none led to a completely satisfactory method (Refs. 8-14).

Stamm (Ref. 8) carried out the $KMnO_4$ oxidation in alkaline solution preventing the precipitation of MnO_2 by addition of a barium salt, thus preventing interference of the brown MnO_2 precipitate with the endpoint. Benson and Hicks

(Ref. 9), in their study of pollution in sea-water, used the Zimmerman Reinhardt procedure to obtain more reproducibile results in their titration of the excess permanganate. Haupt (Ref. 10) examined the wastes from paper pulp factories using acid permanganate, attempting to correlate them with BOD results. Not surprisingly, the chemical results were much higher than those obtained from the BOD test, since cellulose resists attack from both bacteria and dissolved oxygen.

Matsubara (Ref. 11) reported dependence of permanganate values on a variety of factors, including length of boiling, permanganate concentration, and state of hydrolysis (*saponification*) of fats or oils analyzed. Lovett (Ref. 12) confirmed the dependence of permanganate analyses on concentration. Koshkin and Karasik (Ref. 13) determined excess permanganate titrating with oxalic acid at boiling bath temperature, and Shutkovskaya (Ref. 14) compared the permanganate color of heated solutions with standard colored glass plates, after 5 minutes.

1.3 Other Oxidants

Of the numerous oxidizing agents available, only four have been used to any appreciable extent in the determination of the oxygen-consuming power of wastes; they are: ceric sulfate, $Ce(SO_4)_2$; iodic acid, HIO_3; potassium dichromate; and potassium permanganate. The latter appeared as the recommended method in earlier editions of Standard Methods (Ref. 6, p. 122) but is no longer recommended for use in the United States.

1.3.1 Iodic Acid Oxidation

In the iodic acid oxidation the sample is digested in a Kjeldahl flask with standard iodic acid in H_2SO_4 heated to 190°C in a wax bath for 35 minutes after the mixture has stopped boiling. For wastes containing volatile acids the mixture is refluxed for an hour in lieu of the digestion process. The flask is then cooled and the liberated iodine steam distilled. Potassium iodide is added to reduce the unused iodate in the flask and the free iodine formed titrated with sodium thiosulfate ($Na_2S_2O_3$) solution in the presence of a starch indicator.

While the iodic acid method was the most time-consuming of those studied, agreement between replicate samples was good and approached more nearly the theoretical values obtained in the oxidation of pure organic standards.

1.3.2 Sodium Hypochlorite/Permanganate Ratio

Sodium hypochlorite (NaOCl) determined at 3 min and 4 hrs, has proved useful in the differentiation between animal and vegetable pollution when compared with permanganate (Ref. 15). This can be extremely useful in identifying a discharge and locating the source of pollution. Gibson has shown that when the 4 hr ratio hypochlorite/$KMnO_4$ is less than 1.0, the pollutant is largely of vegetable origin. Conversely, for ($NaOCl/KMnO_4$) > 1.0, animal matter is the chief pollutant. Table 4 below lists examples of wastes from animal and vegetable sources which may be differentiated on the basis of their $NaOCl/KMnO_4$ ratios.

Table 4
The $NaOCl:KMnO_4$ ratio for various wastes and polluted waters (Ref. 7, p. 115).

Wastes, etc., of vegetable origin ($NaOCl:KMnO_4$ *ratio* <1·0)	*Wastes, etc., of animal origin* ($NaOCl:KMnO_4$ *ratio* >1·0)
Paper making wastes	Sewage and Sewage effluents
Calico printing wastes	Farm drainage
Cotton bleaching wastes	Piggery wastes
Brewery wastes	Dairy wastes
Vegetable canning wastes	Tannery wastes
Vegetable pickling wastes	Rivers polluted by any of the above wastes
Pea vining wastes	
Coal washing effluents*	—
River waters polluted by any of the above wastes	— —
Peaty river waters	—

* Coal-dust can be regarded as well-decomposed vegetable matter.

It is often possible to shorten the Gibson hypochlorite procedure using 3-min instead of 4-hr ratios, but less reliable conclusions result.

Gibson's generalization does not hold for certain sewage sludges (e.g., activated sludge, digested sludge, and Imhoff tank sludge) which gives ratios of less than 1.0, thus behaving as though they were of "vegetable" origin.

2. Theory of COD Measurement

As with all *oxygen demand (OD)* parameters, COD measurement is based on the reduction of the oxidant by the sample and this, in turn, is interpreted as reflecting sample carbon content. However, this assumption is a valid one only in the absence of other reducing substances (see section 4).

Whatever the nature of the OD test, at its conclusion the system will be stabilized in a lower (final) energy state as compared thermodynamically with its initial state. For a chemical system, less carbonaceous material will remain in the final state than for a biochemical test system, thus providing a better approximation to the total carbonaceous matter *initially* present. By contrast, the biochemical system measures only the *biodegradable* portion of the organic material initially present.

It should further be noted that, given a detailed knowledge of the oxidizable organic constituents present in an effluent, it is possible to calculate its total oxygen requirement theoretically. This quantity, known as the *ultimate oxygen demand (UOD)*, has been determined from the equation (1) below:

$$UOD = 2.67C + 4.57N, \text{ where} \qquad \text{(Eq. 1)}$$

C = the organic carbon content of the effluent, and

N = the sum of ammoniacal and organic nitrogen.

In the presence of other elements contributing to the OD of the system (e.g., H, S, and/or P), this equation must be modified for greater accuracy. Similarly, organically bound oxygen must also be considered in the equation (Refs. 2, 16).

2.1 Chemical Oxidation of Carbon Compounds: Oxidation-Reduction Equations

While it is not possible to write a simple numerical expression for the oxidation of all organic compounds using either acid dichromate or acid permanganate reagents, the illustrative examples below should provide a basic explanation of the chemistry involved in the dichromate (and permanganate) methods of COD determination of organic (*carbonaceous*) pollutants.

2.1.1 Acid Dichromate Oxidation

One of the classical tests for *ethanol* (ethyl alcohol)† consists of warming the alcohol with a solution of *sodium dichromate* ($Na_2Cr_2O_7$) in sulfuric acid (Ref. 17). Under these conditions, ethanol is oxidized to *ethanal** (acetaldehyde†), the yellow dichromate solution is reduced to a green solution (chromic ion, Cr^{+++}), and the aldehyde may be recognized (a) by its fruity odor or (b) alternately by its reducing action on filter paper impregnated with an ammoniacal silver nitrate solution. In the latter instance silver ion is reduced to free silver producing a dark stain on the paper: $Ag^+ + e \rightarrow Ag^o$.

The oxidation of the ethanol to ethanal may be expressed by the following equation:

$$\underset{\text{ethanol}}{3C_2H_5OH} + \underset{\text{sodium dichromate}}{Na_2Cr_2O_7} + \underset{\text{sulfuric acid}}{4H_2SO_4} \rightarrow$$

$$\underset{\text{ethanal}}{3CH_3CHO} + \underset{\text{chromic sulfate}}{Cr_2(SO_4)_3} + \underset{\text{sodium sulfate}}{NA_2SO_4} + 7H_2O \qquad \text{(Eq. 2)}$$

The addition of silver sulfate (Ag_2SO_4) under reflux conditions in the presence of concentrated H_2SO_4 catalyzes the further oxidation of the alcohol (probably through the acetic acid stage) to carbon dioxide and water (Ref. 18).

$$C_2H_5OH \xrightarrow[Ag_2SO_4 \text{ catalyst}, \Delta]{H_2CrO_4, 2[O] \text{ (chromic acid)}}$$

$$[CH_3CHO \rightarrow CH_3COOH] \rightarrow 2CO_2 + 3H_2O \qquad \text{(Eq. 3)}$$

Table 5 (Ref. 19) compares the efficiency of oxidation of typical organic compounds in the absence or presence of Ag_2SO_4. It is clear that straight chain acids (including amino acids) and alcohols are oxidized more completely in the presence of the catalyst. Particularly striking is the case of the highly oxidation-resistant acetic acid which may be oxidized to near completion in the presence of Ag_2SO_4. Oxidation-resistant aromatics such as benzene and toluene, as well as the *heterocyclic* aromatic compounds such as pyridine, are not significantly affected by the catalyst (Ref. 19).

2.1.2 Permanganate Oxidation

In acid solutions permanganate ion (MnO_4^-) is reduced to the manganous state (Mn^{++}). This is the basis of a standardization method for $KMnO_4$ solutions involving oxalic acid or sodium oxalate in acid solution:

$$\underset{\substack{\uparrow\text{(gain)}\\ 5\varepsilon}}{2MnO_4^-} + \underset{\substack{\downarrow\text{(loss)}\\ 2 \times 1\varepsilon}}{5C_2O_4^=} + 16H^+ \rightarrow 2Mn^{++} + 10CO_2 + 8H_2O \qquad \text{(Eq. 4)}$$

In equation 4 a formal charge of +3 on each carbon may be assumed for the oxalate ion, $C_2O_4^=$. This is more apparent if the ion is

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†Classical nomenclature

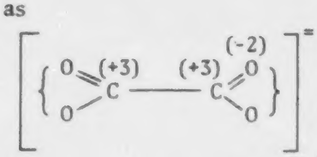
*IUC nomenclature. The root name is derived from the parent hydrocarbon -- in this instance *ethane*, with substitution of the appropriate ending (e.g., *ol* for the alcohol and *al* for the *al*dehyde).

Table 5

Effect of Addition of Silver Sulfate on Dichromate Oxygen Consumed (Ref. 19, p. 795)

Compound	Per Cent of Theoretical Oxidized Without Ag_2SO_4	With Ag_2SO_4
Acetic acid	2.4	95.1
o-cresol	83.2	95.8
Ethyl alcohol	29.7	80.1
Glutamic acid	63.9	100
Lactic acid	45.4	82.7
Sodium stearate	74.2	91.7
Benzene	7.8	8.1
Pyridine	1.3	0.8
Toluene	21.4	22.5

pictured as



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wherein the electron pairs are visualized as in closer proximity to the more *electronegative* (i.e., electron-attracting) oxygen atoms. If the oxygens are assumed to bear their usual charge (-2), then each carbon must be assigned a formal charge of +3 in order for the oxalate ion to be divalent (-2). Thus in equation 4 above, each carbon will lose one electron in going to CO_2, while the Mn (+7) in the permanganate radical will gain 5 electrons. This is indicated by the up (↑, gain) or down (↓, loss) direction of the arrows in the equation.

As with the acid dichromate reaction discussed earlier, the acid permanganate reagent oxidizes straight chain alcohols such as ethanol incompletely to the aldehyde stage rather than all the way to CO_2 and water.

3. Definition

Chemical oxygen demand (COD) is defined as the amount of oxygen in mg/l consumed under specified conditions in the oxidation of organic and oxidizable inorganic substances in wastewater, corrected for the influence of chlorides (Refs. 20, 21).

3.1 Dichromate Oxygen Demand

Dichromate value (British : Ref. 2, p. 687) is essentially synonymous with *Dichromate Oxygen Demand* (American) and this latter term is in turn now used interchangeably with COD in the U.S. (Ref. 22).

Dichromate value is defined as "the number of milligrams of oxygen absorbed from standard dichromate/liter of sample" (Ref. 2)[a] Dichromate oxygen demand has already been defined above (as COD).

3.1.1 Conditions of the Dichromate OD Method

The analysis is carried out under acid conditions (50% by volume H_2SO_4), employing 0.25 N $K_2Cr_2O_7$. Mercuric sulfate (0.4 gm $HgSO_4$/40 mg Cl^-) is added to complex the chlorides, and Ag_2SO_4 previously dissolved in concentrated H_2SO_4 (reagent grade) is used to catalyze the oxidation of the more resistant organics. Since the oxidation is carried out at reflux temperature, no temperature control is required (Ref. 2, 5- section 220).

a) In the *absence* of chlorides, samples with DOC values of 50 mg/l or more may be analyzed with the concentrated dichromate solution (0.25N). For more dilute samples an alternate procedure using 0.025 N dichromate solution is recommended (Ref. 5, p. 498).

b) When chloride is *present* this method is applicable to samples with an oxygen absorption at least 1/4 as great as the $[Cl^-]$ in mg/l.

The method is broadly applicable. Certain nitrogen compounds (e.g., urea) interfere, as will large amounts of chloride ion (i.e., $[Cl^-] \gg 4\times$COD value). The dichromate procedure is described in greater detail in section 5 of this chapter and in Ref. 2, p. 687, and 5, Sec. 220-4a.

4. Factors Influencing the Dichromate Value

A number of factors influence the dichromate value obtained. Thus the presence of chloride ion, which is oxidized by acid dichromate, enhances the dichromate value. On the other hand, certain aromatic organic structures (benzene, pyridine, toluene) resist dichromate oxidation, even in the presence of a silver sulfate (Ag_2SO_4) catalyst.

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[a] see footnote, p. 9

4.1 Chloride

Chloride, a common constituent of natural waters, is oxidized by dichromate. Moore and coworkers at first recommended a correction based on 100% oxidation of the chloride (Ref. 3). However, at high chloride concentrations, AgCl precipitates in a form which dissolves slowly, requiring prolonged reflux periods. Filtration of the precipitate results in the loss of colloidal organic matter thus reducing oxygen absorption (Ref. 23). Table 6 lists OA data for substances typically found in industrial effluents, showing the effects of chloride addition, correction for chloride and removal of chloride by precipitation. The reduction in OA value in the latter instance is evident.

In the absence of Ag^+, sodium chloride (NaCl) solution showed maximum, albeit incomplete, oxidation in 1/2 hr. when solutions of various NaCl concentrations were refluxed with acid dichromate solution and then back-titrated with ferrous ammonium sulfate solution. Table 7 shows the results of these experiments.

The findings of Cameron and Moore clearly indicated that incomplete oxidation of chloride at high concentrations will lead to low OA values. Thus, if the true oxygen equivalent of Cl^- in solution is $\underline{C}$ and $\underline{S}$ the OA value of the organic pollutant, then

$\frac{C}{S} \times P$ = the error in observed OA for % error
$\underline{P}$ incurred by assuming 100% oxidation of Cl^-.

For N/8 dichromate Cameron and Moore (Ref. 23) recommend that the $[Cl^-]$ should not exceed 4 times the OA values of the organic pollutants, if the latter are between 250 and 500 mg/l and total OA is to be within 5% of the true value. When $[Cl^-]$ is 10,000-20,000 mg/l (OA equivalents 112-224 mg/l), the errors incurred might constitute a significant fraction of the OA values for the organic pollutants, leading to low results (see expression above). Thus, alanine and lactic acid both showed severe depression of OA at high Cl^- concentration (~12,000 mg/l).

4.2 Oxidation of Nitrogenous Pollutants in the Presence of Cl^-

In a preliminary experiment with urea, Cameron and Moore found that oxidation of this natural constituent of domestic sewage underwent direct oxidation by dichromate in the absence of Cl^-:

$$NH_2CONH_2 \xrightarrow{3[O]} CO_2 + 2H_2O + N_2 \qquad \text{(Eq. 5)}$$

However, the reaction was enhanced by the presence of chloride in contrast to the inhib-

Table 6

Results for Oxygen Absorbed with Added Chloride (Ref. 23)

Compound	O.A. value, p.p.m.	Chloride added, p.p.m. of oxygen absorbed	Oxygen absorbed with correction for chloride, p.p.m.	Oxygen absorbed with precipitation of chloride, p.p.m.
Cresylic acid	400	400	400	405
Soap	360	800	356	140
Soap	740	800	732	350
Soap	300	400	296	160
Glue	190	500	182	137

Table 7

Oxidation of Chloride in Absence of Silver (Ref. 23)

Chloride taken, ppm	Equivalent volume of N/8 $AgNO_3$, ml	Volume of N/8 $K_2Cr_2O_7$ added, ml	Volume of N/80 $Fe(NH_4)_2(SO_4)_2$ required, ml	Oxidation %
225	1.25	2.0	6.3	109.7
558	3.15	5.0	18.75	99.2
1058	6.10	10.0	40.10	98.1
2112	11.90	15.0	34.40	97.4
4224	23.80	30.0	67.90	97.4
5310	29.90	40.0	118.75	94.0

iting effect of Cl^- on lactic acid and alanine. The authors postulated a possible intermediary role in which Cl^- was itself oxidized to free chlorine by the dichromate, the free Cl_2 formed in turn oxidizing urea, etc. By this mechanism it was possible to explain the dependence of urea oxidation on the presence of Cl^- in the absence of any Cl^- concentration dependency (Table 8).

Table 8

Oxidation of Urea in Presence of Chloride
25 ml of N/8 $K_2Cr_2O_7$ ≡ 5.2 mg of urea
(Ref. 23, p. 681)

Chloride present, p.p.m.	Total volume of N/8 $K_2Cr_2O_7$, ml	Absorption as volume of N/8 $FeSO_4$, ml	Oxidation of urea, %
266	24·5	6·5	52
639	28·6	8·5	68
1278	32·2	9·7	77
6327	60·7	7·14	57
Nil	25·0	4·2	33·6

Although there are a number of possible routes for the oxidation of organic nitrogen by Cl_2, it is assumed that in each case a trivalent N atom is involved. Thus the correction is based on:

$$1 \text{ ml } \frac{N}{8} K_2Cr_2O_7 \equiv 0.5833 \text{ mg } N^{\ddagger} \qquad \text{(Eq. 6)}$$

This correction is only approximate, since not all of the nitrogen will be oxidized by this route, some of it being oxidized directly by the reagent (see Eq. 5, above).

4.3 Oxidation of Organically Bound Chlorine Compounds

In the case of ring and chain compounds containing organically bound chlorine, the percent oxidation obtained varied with structure. Table 9 illustrates the negligible effect of Ag^+ as an oxidation catalyst in all but one (chlorobenzene) of five compounds studied.

5. Procedure: COD Test

5.1 Dichromate Method: Summary

The test is based on the susceptibility of most organic compounds to a boiling mixture of chromic and sulfuric acids. An excess of potassium dichromate ($K_2Cr_2O_7$) in sulfuric acid (H_2SO_4) is employed to oxidize the sample at reflux temperature. Residual dichromate is titrated with ferrous ammonium sulfate [$Fe(NH_4)_2(SO_4)_2$] in the presence of ferroin indicator and the oxidized organic matter calculated in terms of *oxygen equivalents (OE)*. The potassium dichromate consumed and the OE of the sample are related by a proportionality factor. Chemical Oxygen Demand is calculated using the following equation:

$$\text{COD (mg/1)} = \frac{(a-b)N \times 8{,}000}{\text{ml sample}}, \text{ where} \qquad \text{(Eq. 7)}$$

COD = Dichromate Oxygen Consumed

(a-b) = the difference in $Fe(NH_4)_2(SO_4)_2$ *titre* of blank and sample

N = normality of $Fe(NH_4)_2(SO_4)_2$ used.

Mercuric sulfate (0.4 gm) is placed in a 250 ml Erlenmyer flask provided with a ground glass (24/40) neck. The sample (20 ml or a suitably diluted aliquot of the same volume) is mixed with the mercuric sulfate ($HgSO_4$). Ten ml of the standard $K_2Cr_2O_7$ (0.250 N) solution and pumice granules (or glass beads) previously heated to 600°C for an hour are added and the flask fitted with a condenser. Sulfuric acid (30 ml) containing Ag_2SO_4 (22g/9 lb bottle) is gradually introduced through top of the condenser. During addition of the acid the assembly is swirled for *thorough mixing before heating*. This is to avoid *local superheating* of the unmixed H_2SO_4-Ag_2SO_4 solution which is of sufficient density to collect at the bottom of the flask -- in which case it may build up a high enough local vapor pressure to be blown out of the condenser. The mixture is then refluxed for 2 hours.

Table 9
Oxidation in the Presence of Organically Combined Chloride
(Ref. 23, p. 681)

Compound	Oxidation with silver absent, %	Oxidation with silver present, %
Carbon tetrachloride	6·4	6·4
Trichloroethylene	20·0	20·0
Benzoyl chloride*	94·3	94·5
Benzyl chloride	65·2	62·4
Chlorobenzene	12·0	25·6

* Owing to hydrolysis this test becomes in effect a test of benzoic acid and hydrochloric acid.

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‡At wt. of N = 14.008/3 = 4.669 equivalent wt. X 0.125 = 0.5836 mg N/ml reagent

After the reflux period the mixture is diluted to ~150 ml with distilled water, cooled to room temperature, and the excess dichromate present titrated with a standard ferrous ammonium sulfate solution (Ref. 5, Sec. 220-3 Reagents), after the addition of 2 to 3 drops of ferroin indicator solution. For best results the same quantity of indicator should be maintained from sample to sample. The color change at the endpoint is a sharp transformation from blue-green to reddish brown.

A blank is treated in an identical manner and the COD calculated from equation 7.

Notes:

1) The quantity of $HgSO_4$ recommended will complex 40 mg of Cl^- (2000 mg/l) when the volume of sample is 20 ml. In the presence of a greater [Cl^-] than the above, sufficient $HgSO_4$ is added to maintain a 10:1 ratio, $HgSO_4$:Cl^-. Appearance of a small precipitate for the larger quantities does not interfere in the dichromate method.

2) The standard reflux time of 2 hr may be reduced for wastes which develop their maximum COD values sooner.

3) Table 10 (Ref. 5, p. 498) lists recommended ratios of reagent quantities and normalities with size of sample. For larger samples, a 500 ml erlenmeyer flask is used for refluxing the sample, so that it may be titrated *in situ*.

4) An alternate procedure employing 0.025 N dichromate reagent and 0.01 N ferrous ammonium sulfate reagent is given in Ref. 5, section 220-4C, p. 498. Some hard-to-digest volatiles may be lost in this procedure, and the increased volumes used may reduce effectiveness of $HgSO_4$ as a complexing agent for Cl^-.

5.1.1 DOC Method Precision and Accuracy

In a test by 74 laboratories of unknowns containing potassium acid phthalate ($KHC_8H_4O_4$) the following precisions were obtained (Table 10).

Table 10 (Ref. 5, p. 498)

COD (mg/l)	Chloride (mg/l)	Standard Deviation	Coefficient of Variation (%)
200	0.0	±13	6.5
160	100.0	±10	6.5
150	1,000.0	±14	10.8

Moore and coworkers have found 95 to 100% of the theoretical oxidation values for a large number of organic compounds. This excludes the stable aromatics such as benzene and toluene and the nitrogen heterocyclic, pyridine, which are not oxidized in the standard dichromate procedure.

A more complete discussion of the dichromate oxygen demand method is found in Standard Methods, 13th ed. (section 220, pp. 495-9, inclusive).

5.1.2 Dichromate Oxidation: Advantages and Disadvantages

A. Advantages

1) Results obtained with the dichromate method are generally closer to theoretical than the permanganate test (Ref. 2).

2) The dichromate method requires considerably less time (2 hrs max) than the permanganate test.

3) Since the DOC test is carried out at boiling temperature, there is no error due to temperature difference and no need for temperature control.

4) The apparatus required, while slightly more complicated than for the permanganate test, is readily available in any routine laboratory (Ref. 2).

5) For a given effluent, the BOD/COD ratio may be sufficiently correlated so that the chemical data may be used in process and treatment-plant control.

B. Disadvantages

1) Chloride may introduce error not readily corrected if the Ag_2SO_4 is added initially. This may be circumvented by dichromate oxidation of the chloride prior to addition of the Ag_2SO_4 oxidation catalyst.

2) When chloride and nitrogenous compounds are present simultaneously the error correction becomes more difficult, since the nitrogen may be oxidized by two different paths: directly and via liberated Cl_2.

3) Not all organics are oxidized by dichromate reagent, even in the presence of Ag_2SO_4 catalyst. Aromatic compounds such as benzene and the nitrogen heterocyclics related to pyridine resist oxidation in the standard procedure (Ref. 5).

4) The method does not differentiate between biochemically stable and/or unstable organic pollutants.

5.2 COD: Sampling

In general, COD sampling recommendations are similar to those for BOD; namely,

a) Unstable samples should be tested immediately.

b) Care should be taken to insure representative sampling as outlined in the BOD section. Settleable solids should be dispersed throughout the aliquots taken by prior homogenization of the sample.

c) In case of unavoidable delay in analysis, the sample should be preserved by the addition of sulfuric acid.

d) For samples with a high COD, volumetric dilutions should be made to avoid the inherent analytical errors in the measurement of small volumes.

e) Samples should be collected in accordance with ASTM methods D 1496: Sampling Homogeneous Industrial Waste Water (Ref. 24).

For more detailed discussions of OD sampling procedures in this volume, the reader is referred to the DO and BOD chapters' sections on Sampling.

5.3 Permanganate Value: "Oxygen Absorbed"[a] from Acid $KMnO_4$ Solution

The usual concentration of $KMnO_4$ reagent is N/80. However, in the case of some trade wastes N/8 reagent is recommended (Ref. 2, p. 691). The standard time for the $KMnO_4$ test is 4 hr, with the 3-minute $KMnO_4$ test used as a guide to the nature of the waste.

The volumes of samples are adjusted so that the same amounts of reagent permanganate and H_2SO_4 may be used throughout, with the volume (∿50 ml) of $KMnO_4$ solution adjusted so that ca. 50% unused reagent remains at the end of the test.

Where small sample volumes (e.g., high COD) are indicated, it is recommended that a larger volume of a suitable dilution be used in order to be certain that the suspended solids are uniformly distributed.

5.3.1 Reagents

For a detailed description of reagent preparation, the reader should consult Ref. 2, pp 689-90. In addition to the N/80 permanganate solution, the following reagents are used in this method:

a) Potassium iodide (KI) solution (10% w/v). This must remain colorless (i.e., free of iodine). It is stored in an amber bottle.

b) Potassium iodate (KIO_3) solution (N/40), pre-dried at 120°C.

c) Sodium thiosulfate ($Na_2S_2O_3$, ∿N/4), prepared from the pentahydrate, $Na_2S_2O_3 \cdot 5H_2O$ and copper-free, freshly-boiled distilled H_2O. The solution is stabilized by the addition of $CHCl_3$ (1 ml), or alternately, 10 mg of mercuric iodide (HgI_2). Kept in the dark, this reagent is reasonably stable but requires frequent standardization against the iodate solution.

d) Sulfuric acid (1:4 dilution).

e) Starch indicator: may be freshly prepared or stabilized with HgI_2 (10 mg/gm of soluble starch) or thymol (0.1 gm/gm of soluble starch).

5.3.2 "Permanganate Oxygen Absorbed"[a]: Procedure

A. 4-hour test

Ten ml of 1:4 sulfuric acid and 50 ml of N/80 $KMnO_4$ are measured into a 12 oz glass stoppered (G.S.) bottle. Distilled water is added so that the combined volumes of the water and effluent when added will add up to 100 ml and the mixture is incubated at 27°C. The effluent, also at 27°C, is then added to the above mixture containing the acidified, diluted oxidant, and the whole is mixed by a gentle rotation of the bottle. The solution (or suspension) is incubated at 27°C for 4 hours. (If solids are present, the sample is re-mixed at least every hour.)

At the end of 4 hours, 5 ml of KI solution, or approximately 0.5 gm KI, are added, mixed or dissolved, and the solution titrated with N/80 $Na_2S_2O_3$. As the endpoint is approached, 2-3 drops of the starch indicator solution are added and the titration continued to the first disappearance of blue color, ignoring the reappearance of any blue color on standing.

A blank determination is put through the same procedure.

Calculation of the 4-hr permanganate value is made using expression below:

$$\frac{[(\text{Vol. N/80 } Na_2S_2O_3\text{, blank}) - (\text{Vol. N/80 } Na_2S_2O_3\text{, sample})]\text{ ml} \times 100}{\text{Total vol. sampled (ml)}} = \text{4-hr. } KMnO_4 \text{ value, mg/liter} \qquad \text{(Eq. 8)}$$

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[a] This terminology is misleading, since the sample does not absorb oxygen from the reagent. See Sections 1.2 and 2.1.2.

B. 3-minute test

This procedure is essentially the same as in A above: the sample and reagents are prewarmed to 27°C, mixed and maintained at 27°C for exactly 3 minutes, and titrated.

5.3.3 Permanganate OA: Interferences

a) *Nitrite* will reduce permanganate. A correction may be made for its interference by subtracting the factor nitrite N x 1·4.* For significant amounts of nitrite, the latter is best destroyed prior to analysis by the addition of 1 gm of urea to the acidified sample (and blank). The treated sample is allowed to stand for 5 min before proceeding with the $KMnO_4$ addition.

b) *Chromates* are reduced by KI in acid solution, and will therefore decrease the $KMnO_4$ value. A correction for this error may be made by carrying out a preliminary titration with thiosulfate reagent prior to addition of the permanganate solution and adding the equivalent OA value to the observed permanganate obtained (Ref. 2).

6. Oxygen Demand Index (ODI)

The COD method was developed as a relatively rapid OD technique for use in conjunction with the time-consuming BOD method (see Introduction to this chapter and Section 3, BOD). However, the standard COD procedure is still a relatively lengthy one for effective monitoring of the frequently rapidly changing OD conditions of receiving and effluent wastewaters. To cope with this problem, the Oxygen Demand Index was introduced by Westerhold (Ref. 25). This is a rapid COD test based on the Standard Methods procedure. However, instead of refluxing for two hours, the sample and reagent mixture are heated in a test tube (T.T.) at boiling water temperature for only twenty minutes and titration is replaced by the more rapid colorimetric measurement of green chromic ion at 600 mμ (Ref. 26). The ODI is then read off a calibration curve based on glucose. The latter curve is obtained by comparing the percent transmission of the oxidized standard glucose solution with its known 5-day BOD value. Sample readings are made with reference to a similarly treated distilled water blank.

Shriver and Young (Ref. 26) concluded from their examination of wastewater samples collected from a number of sources that

1) the ODI test furnishes an approximate BOD value of wastewater simply and rapidly provided that sufficient data are collected at each sampling point.
2) Precision for the ODI test is comparable with that reported by a number of workers for COD.
3) Correlation of BOD-ODI values is poorer than for other BOD-COD tests, but better than BOD-TOC correlations obtained.

Reynolds and Goellner (Ref. 27) concluded from their statistical evaluation of the ODI method that it did indeed give higher values than BOD_5 as had been reported previously. They further expressed the opinion that the "use of elaborate instrumentation or gadgetry being marketed today" should not be recommended to "the less well informed operational personnel."

7. Correlation of COD with Other Parameters

The literature abounds with attempts to correlate COD with BOD, TOC (Total Organic Carbon), TOD (Total Oxygen Demand), and variants of these parameters. Section 3 of the BOD chapter dealt with the significance and limited validity of BOD-COD comparisons. Since TOC and TOD-related parameters involve instrumentation, these comparisons will be discussed in the appropriate sections of the following chapter on Instrumentation of Oxygen Demand Parameters.

8. Criteria

There are as yet no separately promulgated COD standards. Recommended criteria vary with the use for which the water is intended (BOD, section 5, DO, section 4). Thus, the following limits "Oxygen Consumed" values were suggested for boiler feed waters:

Table 11

Recommended Oxygen Consumed Limits for Boiler Feedwaters (Ref. 28, p. 233)

Pressure in Psi	*Oxygen consumed, mg/l*
0-150	15
150-250	10
250-400	4
400 and over	3

For potable waters the 1962 USPHS standards based on the *Carbon Chloroform Extract (CCE)* procedure is still in effect, with the recommended limit set at 200 μg (or 0.2 mg) per liter. The recent development of a new minisampler and a micro-extraction technique is expected to result in a lowering of the recommended CCE limit to 100 μg/l.* It is reasonable to expect that COD methodology will result in attempts to correlate the more rapid COD techniques with the CCE method.

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*For method of determining low (i.e., <2 mg/l) and high concentrations of nitrite N in solution, see Ref. 7, pp. 38-9.

9. COD: Summary and Conclusions

The COD test has been applied to problems of industrial waste treatment. It has also found use in the areas of process control (Refs. 3, 18, 25, 26, 27).

Chemical oxygen demand has been used in the detection of toxic conditions interfering with the normal BOD test, and for the detection of biologically resistant organic pollutants. Used as an adjunct to the BOD test, COD can assess the biological stability of an aquatic system, often providing a rapid estimate of its BOD. Measurement of COD provides an estimate of the total organic content of the sample -- not just the carbon portion of it. Thus, compounds containing organically-bound nitrogen, phosphorus or sulfur may also be measured using the COD method.

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*Private communication, J. J. Connors

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INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

H2O-BIO
Instrumentation
August 1974

INSTRUMENTAL MONITORING OF OXYGEN DEMAND AND RELATED PARAMETERS

INTRODUCTION

A successful water quality management program frequently requires continuous quantitative measurements of BOD-related parameters. For these, automated and semi-automated methods have been developed. Some examples of such methods will be discussed in the following section.

As used in this paper the term *automated methods* will refer to those methods employing analytical instrumentation in the continuous (or, at least, semi-continuous) measurement of BOD and related parameters. Any measuring device provided with a *sensor* or transducer, *signal-conditioning* circuitry, and a means of *read-out* constitutes an *instrument*. If the instrument may be used in a continuous or semi-continuous fashion, it will be regarded as an *automatic* instrument. This is an admittedly arbitrary use of the term "automatic", since "continuous" and "automated" are not necessarily synonymous or interchangeable terms. In practice however, this terminology has been found convenient.

A variety of automated instruments and methods now exist for the determination of OD in natural and wastewaters as well as in sewage effluents.

1. Oxygen Demand

Oxygen demand techniques are based either on oxygen consumption or on its equivalent. This is in turn interpreted as reflecting sample carbon content. However, this interpretation is valid only in the absence of other reduced, i.e., oxygen consuming or *oxidizable* substances. Whether the test used is chemical or biochemical, the system will ultimately be stabilized thermodynamically in some lower energy state. When this state is reached for a chemical system, less carbonaceous material will remain. Thus the chemical system provides a better approximation to the total carbonaceous materials originally present, whereas the biochemical test system reflects that portion of the organic material present which was biodegradable and may thus be more representative of the actual processes occurring in a receiving stream or a sewage treatment plant.

2. Chemical Oxygen Demand (COD)

The standard COD test employs a wet chemical oxidation with acid-dichromate and a silver sulfate catalyst. The oxidized solution is then back-titrated with ferrous ammonium sulfate and the dichromate consumption calculated in terms of oxygen (Ref. 1, pp. 290, 495). The oxidation efficiency of the method varies with classes of organic compounds present. Non-carbonaceous constituents (reduced states of N and S), some halides and many metals also react (see H2O-COD, section 3.2).

The COD test has been applied to problems of industrial waste treatment; it has also found use in areas of process control (Refs. 2 - 6 incl.). It has been used in the assessment of toxic conditions interfering with the normal BOD test, and for detection of biologically resistant organic pollutants. Used as an adjunct to the BOD test, COD can assess the biological stability of an aquatic system often providing a rapid estimate of its BOD. Measurement of COD provides an estimate of the *total organic content* of the sample -- not just the carbon portion of it. Thus compounds containing organically-bound nitrogen, phosphorous, halogens and sulfur may be measured using the COD method.

3. COD: Automated Methods

Automated Chemical Oxygen Demand methods may be classified as: a) *wet combustion* or b) *dry combustion* methods. These will be discussed in the following sections.

3.1 Wet Combustion Method

Molof and Zaleiko (Ref. 7) have successfully automated the standard dichromate method (the Technicon Autoanalyzer) extending the utility of the test for routine continuous pollution monitoring, control and testing. Thus, the normal time span for a complete manual COD determination is from 3 - 5 hours, with semi-quantitative results often obtainable in less than 2 hours (see H2O-COD, section 4.1). The automated version of the procedure was designed to provide complete analyses in less than 1/2 hr. (*ca.* 10 min./sample, 10 samples/hr.).

3.1.1 Spectrophotometric Principle

The basis of the procedure is the color change from the *oxidized* state of dichromate (Cr^{+6}, yellow) to the *reduced* state (Cr^{+3}, green) which is measured photometrically.

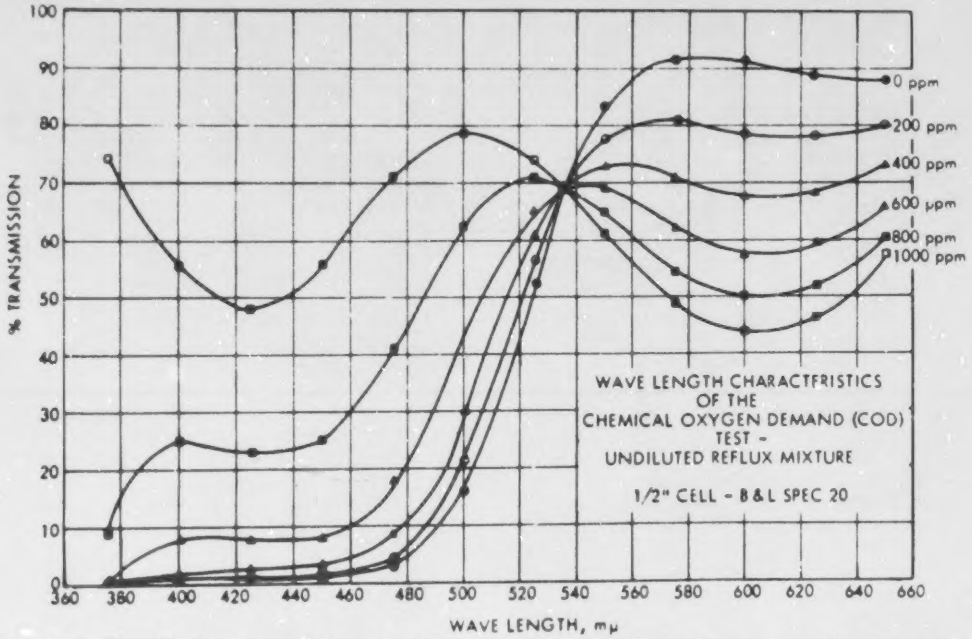

Figure 1. Wave length characteristics of the chemical oxygen demand test. Undiluted reflux mixture (Ref. 7, p. 542).

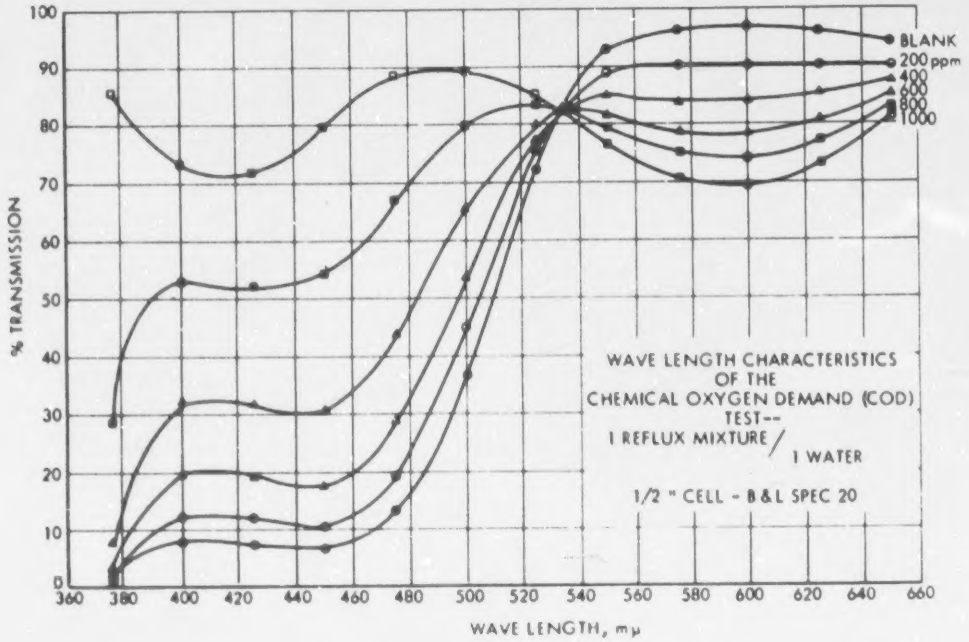

Figure 2. Wave length characteristics of the chemical oxygen demand test. 1 reflux mixture/1 water (Ref. 7, p. 543)

The system presents an interesting example of the existence of two forms of Cr in equilibrium; the sum of the oxidized and reduced forms present constitutes the total amount of Cr in solution. The spectrum obtained thus represents the sum of absorptions of the two states of Cr present in solution.

In Fig. 1 the wavelength characteristics of the undiluted dichromate reflux mixture are shown, revealing the *isosbestic point* characteristic of systems involving equilibria. At this point the sum of the oxidized and reduced forms of Cr is constant (*invariant*), and the curves for all concentrations intersect. For systems containing more than one equilibrium, there will be an equal number of isosbestic points.

The photometric measurement may be made on either side of the isosbestic point which in this instance occurs at 535 mμ. In practice the wavelength 440 mμ was used to measure percent transmission of diluted samples, since at this wavelength *Beers law* was followed for the diluted sample and the difference in percent transmission between oxidized and reduced forms was greater (Fig. 2).

Photometric measurement of COD has been found to yield results comparable with those obtained using the standard dichromate titration technique. It has the further advantages of greater speed in addition to which it requires less skill of the technician. Table 1 compares COD values obtained using colorimetric and titrimetric methods on a variety of waste waters (Ref. 8).

3.1.2 Automated COD: Method and Apparatus

The apparatus consists of (1) a continuous digestion module used in conjunction with (2) a reagent pump, (3) measuring and mixing module, (4) a heating bath, (5) a

Table 1

Comparison of COD Values Obtained by Colorimeter and by Titration
(Ref. 8, p. 925)

No.	Description of Sample	Chemical Oxygen Demand mg/1		$\frac{COD_c}{COD_t}$
		Colorimeter[1]	Titration	
1	Raw Sewage, Stillwater	555 (684)[2]	516 (540)	1.076 (1.267)
2	Primary Effluent, Stillwater	488 (550)	511 (563)	0.955 (0.977)
3	Refinery Waste, Tulsa	5210 (5530)	5256 (5715)	0.991 (0.968)
4	Primary Effluent, Okla. City	693 (470)	662 (430)	1.047 (1.093)
5	Mixed Liquor, Okla. City	2970 (2662)	2965 (3290)	1.002 (0.809)
6	Hardboard, Plant Effluent	1109 (1185)	1090 (1155)	1.014 (1.028)
7	Hardboard, Digester Liquor (1/25 Dil.)	1318 (1489)	1458 (1520)	0.905 (0.979)
8	Hardboard, White Water (1/10 Dil.)	511 (568)	507 (562)	1.008 (1.010)

[1] Values obtained using glucose calibration curve.

[2] Values in parentheses are results obtained using Ag_2SO_4 added at the beginning of the reflux period.

colorimeter and (6) a recorder (see flowsheet, Fig. 3). The waste water may be introduced continuously from the sampler cups or discrete samples (10-20/hr) may be introduced by automatic samplers. Wastewater and dichromate are introduced simultaneously by means of a pump fitted with a flexible tube for each reagent. The use of tubes of calibrated diameter facilitates the measurement of small quantities of reactants into the system. Reagents and sample are mixed in a helical glass coil, heated, and moved on to the digester. In order to prevent the escape of volatiles before oxidation and to provide for the initial digestion of the more easily degradable substances, the heating bath is set at 95-155° with a retention time of ∿ 5 minutes.

The digester itself is a rotating glass helix placed above 2 stages of electrical heaters arranged in series. Internal helix temperatures are controlled by means of two variacs, and the rotation of the helix is at a constant (preset) speed, such that the digestant remains in the helix between 2 to 6 minutes. The mixture volume is a small volume which is distributed throughout the rotating heated helix as a thin film, allowing for rapid heat transfer and efficient digestion of the sample.

After digestion the mixture is pumped, diluted with distilled water, cooled and passed through a continuous flow differential (dual beam) colorimeter, and the electrical signal is recorded as percent transmission (%T) or absorbance.*

A series of standard solutions put through the above procedure provide the

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*absorbance:optical density = -log %T

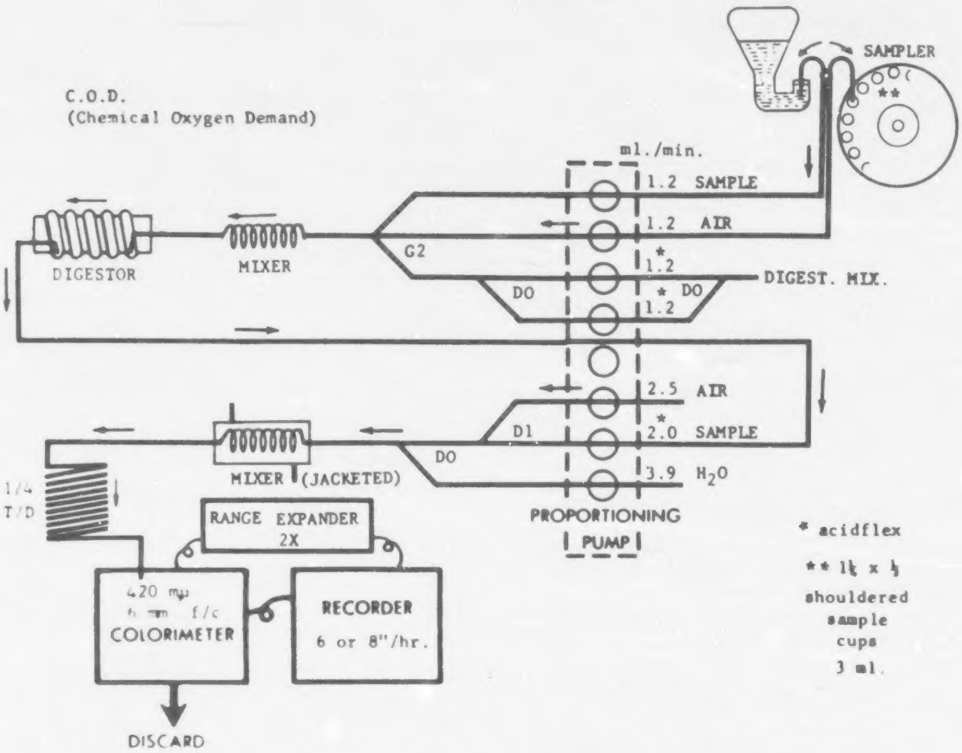
C.O.D.
(Chemical Oxygen Demand)
SAMPLER
**
ml./min.
1.2 SAMPLE
1.2 AIR
*1.2
DIGEST. MIX.
* DO
1.2
DO
G2
DIGESTOR
MIXER
2.5 AIR
*2.0 SAMPLE
3.9 H_2O
D1
DO
MIXER (JACKETED)
1/4 T/D
RANGE EXPANDER 2X
420 mμ
6 mm f/c
COLORIMETER
RECORDER
6 or 8"/hr.
DISCARD
PROPORTIONING PUMP
* acidflex
** 1¼ x ½ shouldered sample cups 3 ml.

Figure 3. Automated COD flowsheet (Ref. 7, p. 545).

conversion data from %T to mg/liter COD. Because of the segmenting air bubbles and continuous flow of oxidant between samples, the system is self-cleaning. Fig. 4 below illustrates typical COD response patterns for two different concentrations of dextrose.

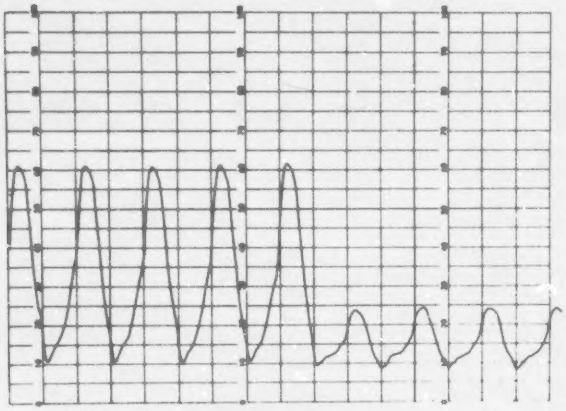

Figure 4. Response pattern for automated COD at two different concentrations (from Ref. 7, p. 546).

Figure 5 illustrates a diagram of a more recent version of the autoanalyzer used for low level COD detection.

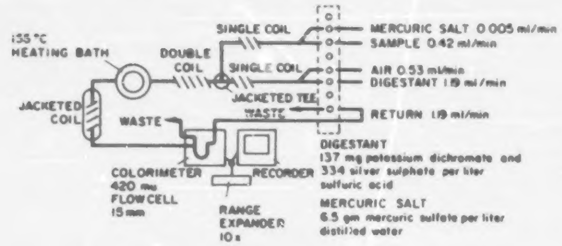
155 °C
HEATING BATH
DOUBLE COIL
SINGLE COIL
SINGLE COIL
JACKETED TEE
JACKETED COIL
WASTE
WASTE
MERCURIC SALT 0.005 ml/min
SAMPLE 0.42 ml/min
AIR 0.53 ml/min
DIGESTANT 1.9 ml/min
RETURN 1.9 ml/min
COLORIMETER
420 mu
FLOWCELL
15 mm
RECORDER
RANGE
EXPANDER
10 x
DIGESTANT
137 mg potassium dichromate and
334 silver sulphate per liter
sulfuric acid
MERCURIC SALT
6.5 gm mercuric sulfate per liter
distilled water

Figure 5. Low level COD detection by use of AutoAnalyzer (Ref. 9).

In another* version of the Automatic COD Analyser, designed for unattended on-line operation, a 10 ml sample is obtained automatically from the sample stream and dispensed into the reaction vessel. Sulfuric acid, potassium dichromate and mercuric sulfate reagents are then added and the solution refluxed for a preset period of from 1/3 to 2 hours. Formation of the green Cr^{+++} is photometrically monitored during the entire heating cycle, the final reading being a measure of the sample's COD (Ref. 10).

3.1.3 Factors Affecting Automated Wet COD Method

In general the same factors affect the oxidative digestion whether the method employed is automated or manual. Silver sulfate catalyzes oxidation of straight chain aliphatics, but has little effect on aromatics such as benzene which resist the reagent.

Silver sulfate precipitates as the halide in the presence of halogen, resulting in incomplete oxidation and low results. In the absence of the catalyst, chlorides are completely oxidized and results can be corrected for chlorides if they are determined separately as well.

Mercuric sulfate ($HgSO_4$) has been used to complex chlorides, thus avoiding the risk of incomplete oxidation and the necessity of analyzing for Cl^- (Ref. 11).

Temperature is an important factor affecting digestion. The acid concentration determines the boiling point of the mixture (and therefore the reaction temperature, ∿ 145°C, in the manual method. This temperature limitation determines the length of time required for complete digestion. Since the automated method is read colorimetrically, the pH limitations imposed when a titration method is used for measurement no longer apply. This allows the use of both high acid concentrations and temperature, shortening the required digestion times (Ref. 12).

3.1.4 Autoanalyzer: Evaluation

A variety of samples, including individual organic chemical compounds and composite waste-stream samples from a treatment plant, were tested by the standard manual and the automated methods. Industrial waste samples were digested for the customary 1 hour for the manual analysis. Results of these comparisons are shown in Table 2. Ballinger and Lishka (Ref. 13) report a precision of ±8% of the accepted value for the manual COD method. The results

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*Formerly marketed by Ionics as the Auto COD Analyzer Model 335.

Table 2

Comparison of Automated with Manual COD (from Ref. 7, p. 547)

Sample Source	AutoAnalyzer COD, ppm	Manual (by Industrial Plant) COD, ppm
Trickling Filter Effluent		
#1	530	540
#2	522	520
#3	770	705
#4	445	385
Activated Sludge Effluent		
A	200	208
B	218	212
Trickling Filter Effluent	430	416
Waste Influent, Raw	3000	2960
	9600	7560
	1700	1960
	4500	4240
	2120	2300
Trickling Filter Effluent with Lower Heat Input to Digester (to Show Temperature Effect)		
F1	435	480
F2	362	415
F3	370	445
F4	252	265

Unpurified U.S.P. Grade Reagents	COD, ppm AutoAnalyzer	COD, ppm Theoretical	Per Cent Recovery	
			AutoAnalyzer	Literature* (Manual)
Ethyl Alcohol 1/2000 dil.	379	994	38.2	29.7
Acetic Acid " "	60	533	11.4	2.4
Lactic Acid " "	243	533	45.6	45.4
Citric Acid " "	393	393.5	100.0	96.8
Toluene 1/4000 "	90	782.5	11.5	14.9
Phenol 1/3000 "	705	678.3	100.0	—

NOTE: Calibration based on fresh Dextrose solution, 440 mμ, 4 mm cell.

*Moore, W.A., et al., (2,3).

obtained for both activated sludge (A.S.) and trickling filter (T.F.) effluents showed good agreement, with differences between the automatic and manual methods averaging less than 5%. The fact that in most instances the automated method gave the higher COD value would indicate that digestion was more complete under these conditions. Reducing heat input resulted in lower automated COD values than for the manual method (loc. cit.).

With influent wastes between 1700-9600 mg/1, the results obtained were similar, albeit not as good (~ 11%). Some of this discrepancy was attributed to sampling problems because of the presence of suspended solids and therefore not directly related to the automation itself. The solution here rests with the use of proper mechanical samplers (Ref. 7).

In a recent evaluation of the methodology employed in the AutoAnalyzerⓉ II system, Tifft & Cain concluded that reproducibility and recovery was excellent, but that not all industrial and municipal wastes yielded the same degree of oxidation as that obtained in the manual procedure (Ref. 14).

3.1.5 Automated Wet COD Method: Summary

Control, monitoring and pollution testing using a continuous, automated COD system is feasible. It is also highly desirable where the quality or safety of streams or plant process control operations are involved. Although automation of COD does not inherently alter the COD test, the substitution of an automated for a manual system will facilitate the maintenance of optimum waste-treatment plant operation. The use of automated COD testing reduces the risk of *shock loading* by furnishing an immediate warning.

Automated wet COD, by substituting colorimetry for titration, further reduces the time required for measurement and eliminates certain disadvantages inherent in any titration technique (e.g., the need for special indicator reagents and subjective error).

3.1.6 Advantages and Disadvantages of the Automated Wet Method for COD

Advantages of the method are:

A. Acceptable precision and much shorter analysis time: the original method required several hours per analysis; the automated method, less than 10 minutes/sample (~ 10 samples/hr). This potential for lower labor input per sample exists where there is a sufficiently large number of samples involved. However, the time-saving and efficiency advantages of automated COD are lost unless a large number of sample measurements or continuous monitoring are required.

The automated method has the disadvantages inherent in the wet method. They are:

A. As in the manual case, automated COD does not differentiate between organic and inorganic reducing species, or between degradable and non-biodegradable organic carbon.

B. There is some continued sensitivity of the procedure to organic structure (e.g., benzene, pyridine, etc.).

C. Automated wet COD analysis requires a high level of technical competence and judgment in carrying out the procedure and interpreting the data.

3.2 Vapor Phase Oxidation: Dry Combustion Methods

Some organic chemicals resist biochemical methods of oxidation; others are resistant to the wet chemical (COD) approach. None resist catalytic combustion which is the basis of the *Total Organic Carbon (TOC)* method discussed in Section 3.2.1 below. Strictly speaking TOC is not an "oxygen demand" method. However, since much of the research carried out with the TOC analyzer has been oriented toward the correlation of this parameter with traditional oxygen demand parameters, it is reasonable to consider the method at this time.

3.2.1 Total Organic Carbon (TOC)

One of the earliest instruments designed for the measurement of the carbonaceous content of waters was described by Van Hall, Safranko and Stenger (Ref. 15). This total carbon analyzer provides a carbon analysis in two minutes and requires only microliter quantities of sample. The procedure entails the injection of a sample by means of a microsyringe into a catalyst-packed combustion tube housed in a high temperature furnace maintained at 950°C. When the carrier gas is pure oxygen, organics are converted to CO_2, H_2O and N_2. On leaving the tube furnace the combined product and sample water is condensed out and the remaining non-condensible gases are passed through the continuous flow sample cell of a nondispersive infrared (NDIR) spectrophotometer sensitized to CO_2. The quantity of CO_2 recorded is proportional to the carbon content of the original sample, and is detected as an electrical imbalance by the CO_2 analyzer (Ref. 16). The flow diagram for a typical Total Carbon Analyzer is shown in Fig. 6.

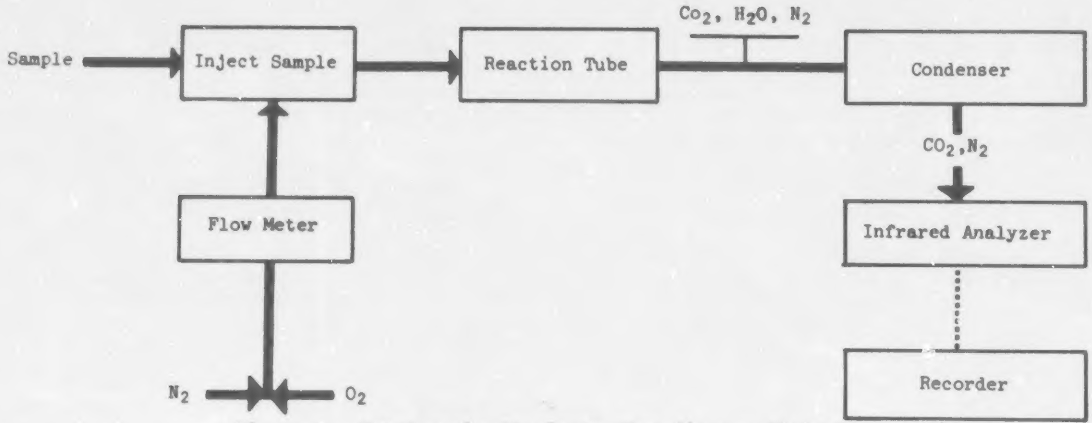

Figure 6. Total Carbon Analyzer flow diagram (Ref.17, p. 130).

This procedure does not distinguish between organic and inorganic carbon, since inorganic carbonates will also yield CO_2 at the elevated temperature. The differention is made by initial acidification and sparging of the sample prior to combustion, or by use of the dual channel analyzer (Ref. 18) described in the following section.

3.2.1.1 TOC Analyzer: Dual Channel System

The TOC system described under 3.2.1 comprises the single channel version which requires prior chemical removal of inorganic carbonate. However, there is also available a dual channel instrument in which a second sample of equivalent size to the first is injected into a flowing air-stream which carries it to a second combustion tube, this one packed with quartz chips wetted with 85% phosphoric acid* and heated electrically to 150°C. At this lower temperature organic compounds are not oxidized, but CO_2 is released from the inorganic carbonates by the acid-treated packing, and the water is vaporized. The steam and CO_2 are swept out of the furnace by the air, steam is condensed and removed, and the CO_2 measured as in the single channel case. Organic carbon is then calculated by difference.

A completely automated version of the TOC instrument has been reported by Boucher and coworkers (Ref. 19). It is similar to the instrument reported by Van Hall et al. (Ref. 15, 20).

The analyzer has two automated features; namely, carbonate is removed via an acidification and nitrogen sparging process, and heterogeneous samples are homogenized in an on-line homogenizer.

3.2.1.2 TOC Procedure: Analytical Considerations

A. TOC Sample Handling

The TOC method was designed for use with true solutions. However suspensions have been analyzed by the use of larger bore syringes. As with BOD and COD analyses, samples must be analyzed quickly or stored at low temperature (∿ 4°C) in the dark. Addition of mineral acid to a pH of 2 inactivates most bacteria. Mercuric chloride has also been employed as a biostat. If the sample is first filtered through a 0.45 μ membrane filter, most of the cellular materials are removed, and the filtrate may then be safely frozen prior to analysis. However, the latter procedure is not recommended for sewage or effluents.

B. TOC Sample Analysis

Since the carbonaceous analyzer measures all the carbon present in the injected sample, prior treatment of the sample will determine the kind of carbon measured by it. In general, there are 3 main classes of carbonaceous materials: 1) soluble organic carbon (i.e., sugars, organic acids, organic bases), 2) insoluble organic carbon such as cellulosic materials, oils and waxes, and 3) other organic matter, soluble or insoluble, present in an adsorbed and/or otherwise entrapped state. Any or all of these classifications may also contain volatile organics. Categories 2) and 3) may be quantified using the carbonaceous analyzer, but rather complex sampling procedures and pretreatment are required.

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*Catalyst packing in the high temperature tube furnace is cobalt oxide-impregnated asbestos.

The TOC analysis of a water sample is generally carried out on the clear supernatant fraction remaining after removal of inorganic carbonate as CO_2 from the acidified sample (HCl, pH 2). This is accomplished by sparging the acidified sample with an inert gas such as water-pumped N_2. Oil-pumped N_2 is not employed for obvious reasons. For non-homogeneous samples a high-speed blender type homogenizer is often used to reduce particle size and homogenize the sample simultaneously. A magnetic stirrer may be used to maintain proper particulate dispersion in the sample so that a representative aliquot is introduced into the syringe. Syringes with a number of different bore sizes are available for use with samples containing suspended solids (70, 140, 400 μ) (Helms, Ref. 28).

In addition to the detailed instructions provided by most instrument manuals, the Federal Water Pollution Control Administration has published a stepwise description of the TOC method applied to both single and dual furnace TOC instruments (Ref. 21).

For further details of sampling, sample preservation and the preparation of standard solutions the reader should consult Refs. 18 and 22.

The following equipment is required for TOC analysis:

a) a precision hypodermic syringe, capacity 0-50 μl

b) a blender

c) a carbonaceous analyzer, single or dual channel type.

C. Packing for the Total Carbon Tube

20 g of $Co(NO_3)_2 \cdot 6H_2O$ (Cobaltous nitrate hexahydrate) is dissolved in 50 ml distilled water and mixed with 15 g long-fiber asbestos in a porcelain evaporating dish. The mixture is evaporated to dryness on a steambath and the dish then placed in a cold muffle and brought up to 950°C and kept at this temperature for 1 to 2 hours. Any large lumps which form are broken up. The combustion tube is then lightly packed with 5 to 6 cm of the catalyst mixture (ca. 1 gm), held in place by small plugs of untreated asbestos. The gas flow rate for the packed tube is then measured at room temperature and at 950°C. The rate should not be more than 20% lower at the elevated temperature.

D. Packing for the Carbonate Tube (Dual Channel System)

A small wad of asbestos or quartz wool is placed at the exit end of the tube and the tube lightly packed with about 10 cm of 6-12 mesh quartz chips. An excess of 85% H_3PO_4 (phosphoric acid) is poured through the packed tube which is allowed to drain in the vertical position.

E. Method

The IR analyzer and recorder are switched on allowing sufficient warm-up time for drift-free operation (about 2 hours).* The total carbon furnace is heated to 950°C; the carbonate furnace, to 175°C. An oxygen flow rate of 80-100 ml/min is maintained through the TC tube. Amplifier gain is adjusted so that a 20 μl sample of the 100 mg/l organic C standard (KH phthalate - $KHC_8H_4O_4$) gives a peak height of approximately 1/2 scale (or an alternate standard concentration may be used, depending on the sample to be measured). For these settings, noise level should be < 0.5% full scale.

Just prior to analysis or calibration, several portions of the selected standards are injected to obtain constant readings.

E-1: Dual channel analyser: Twenty (20) μl each of the organic C standard (and a blank), and of the sample, are successively injected into the system and the peak heights recorded. The recorder pen is allowed to return to its baseline between injections.

Similarly, a series of diluted carbonate standards are prepared, ranging from 20-100 mg of inorganic carbon (IC)/liter.

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*If the analyzer is used every day it may be left on continuously.

The (4 way) valve of the apparatus is then so oriented as to direct gas flow through the low temperature furnace, again adjusting flow rate to between 80-100 ml/min. Again, the baseline is allowed to stabilize. Standard, sample, and water blank are then successively introduced into the low temperature furnace and the peak heights recorded.

3.2.1.3 Precision and Accuracy

On clear samples, or those that have been filtered prior to analysis, a precision of 1 to 2% or 1 to 2 mg/l -- whichever is the greater -- may be attained. Unfiltered samples yield a precision of 5-10% (Ref. 1).

For a single laboratory (Ref. 18), the coefficients of variation at TOC levels of 20 and 30 mg/l were ±3.08% and ±0.02% respectively, when the single channel instrument was employed.

3.2.1.4 TOC: Advantages and Disadvantages

Advantages

The advantages of TOC rest in the following characteristics of the method:

1) TOC analyses are rapid, yielding results in a matter of minutes. The method is particularly useful in process control where even the wet COD method may be too slow in terms of the required response time to a changing process situation.

2) A TOC analysis requires very little sample; 20-50 µl usually suffices.

3) The TOC procedure is generally applicable to organics and relatively specific in nature (Ref. 23).

4) The method is more reproducible than either BOD or COD, displaying an oxidation efficiency of 98 to 100% for a large variety of materials (e.g., acetic acid, arylamines, substituted phenols and pyridine). (Ref. 20).

Disadvantages and Limitations

a) The procedures apply to homogeneous samples only, i.e., those which can be injected into the apparatus reproducibly by means of a syringe. The diameter of the syringe needle limits the size of the particles (Ref. 24). Furthermore it is sometimes difficult to obtain reproducible results from homogenized samples probably because of variation in particle size.

b) TOC measures organic carbon without regard to its biodegradability and this may not accurately reflect true oxygen demand.

c) As a corollary to b), TOC measures only the carbon in organics and does not indicate ecologically important interactions. Thus the value often bears little relevance to the BOD of the system. In general, TOC more nearly reflects the COD than it does the BOD of a system.

d) The method requires a considerable degree of chemical knowledge and skill on the part of the analyst.

e) At the high sensitivity required for potable water, IR analyzer stability has been a problem in the TOC method.

3.2.2 The AquaRator: CO_2D

A variant of the COD analyzer known as the "AquaRator" (Refs. 25, 26) uses oxygen-free CO_2 as the oxidant. Carbon dioxide, deoxygenated by preheating in a carbon furnace (440°C) is then catalytically reacted with the organic sample at ∿ 900°C (Pt gauze cat.), and is itself reduced to CO:

$$C_xH_yN_zO_w + nCO_2 \rightarrow (n + x)CO + \left(\frac{y}{2}\right)H_2O + \left(\frac{z}{2}\right)N_2$$

(Eq. 1)

The CO is detected by means of an infra-red analyzer. For the corresponding oxidation reaction with O_2, Equation 2 may be written:

$$C_xH_yN_zO_w + \left(\frac{v}{2}\right)O_2 \rightarrow x\, CO_2 + \left(\frac{y}{2}\right)H_2O + \left(\frac{z}{2}\right)N_2$$

(Eq. 2)

It can be shown by the stoichiometric comparison of Equations 1 and 2 that $v = n + x$, and that v/2 moles (or v atoms) of oxygen required for the complete oxidation of $C_xH_yN_zO_w$ is equivalent to (n + x) moles of CO resulting from use of CO_2 in the oxidation. A comparison of values obtained with the AquaRator (termed CO_2D values to differentiate them from those obtained in the conventional COD procedure) is shown in Figure 7. With the exception of a number of nitrogen compounds,* the values are comparable to those obtained in standard COD determinations reported (Refs. 25 and 3).

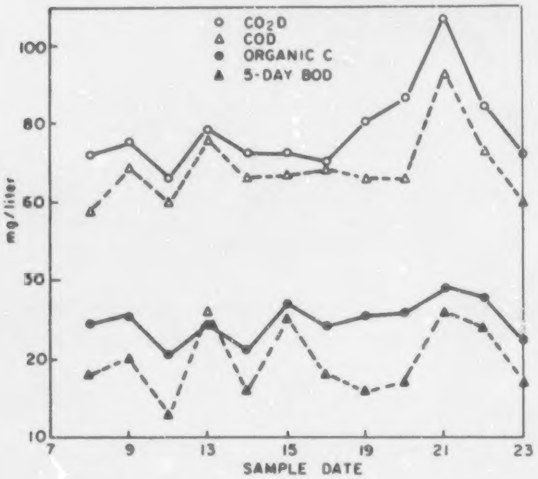

Figure 7. Comparison of CO_2D analysis with the COD, Organic C and 5-day BOD, values obtained on secondary effluent (Ref. 27).

3.2.2.1 CO_2D Analysis Procedure

In practice a 20 µl sample of the wastewater (homogenized, if solids are present) is injected into the instrument by means of a syringe and the sample swept through the (Pt) catalytic furnace by means of a stream of 'bone dry' CO_2 gas. This oxidizes organics to CO and H_2O. The latter is stripped from the mixture by means of a drying tube, the residual products further heated over Pt and the [CO] measured by means of a nondispersive integral IR (NDIR) analyzer. The reading is converted to COD units by means of a standard calibration chart. Figure 8 illustrates the flow diagram of the AquaRator.

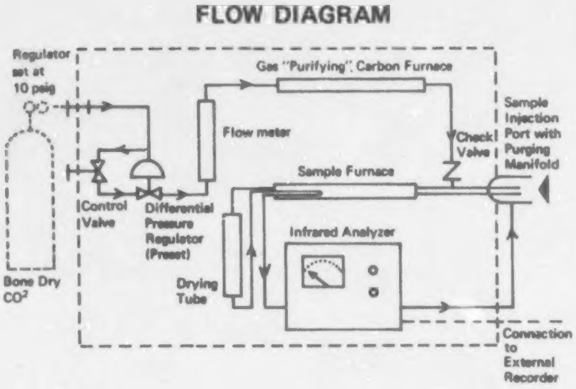
FLOW DIAGRAM
Regulator set at 10 psig
Gas "Purifying" Carbon Furnace
Flow meter
Check Valve
Sample Injection Port with Purging Manifold
Sample Furnace
Control Valve
Differential Pressure Regulator (Preset)
Infrared Analyzer
Drying Tube
Bone Dry CO^2
Connection to External Recorder

Figure 8. Precision AquaRator CO_2D Analyzer (Ref. 26).

3.2.2.2 AquaRator Design and Measurement Capabilities

The WPCA-suggested concentration limits (10 to 300 mg/l) for COD fall well within the purview of the instrument. Precision is good (± 3%) compared with BOD tests which may deviate from one another by as much as ± 15%. Figure 9 below illustrates AquaRator CO_2D values plotted against corresponding COD and five

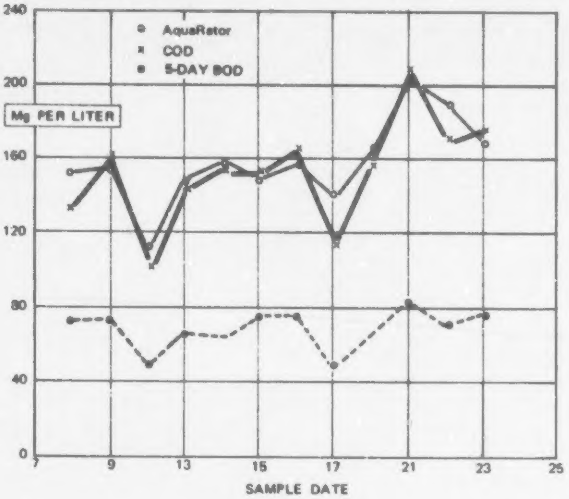

Figure 9. Primary effluent (Ref. 26).

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*See Section 3.2.2.4

day BOD values. Not unexpectedly, the CO_2D values parallel COD and are higher than 5 day BOD values, the latter measuring only those organics which are biodegradable.

3.2.2.3 Advantages of the CO_2D Method

1) The AquaRator is designed for continuous duty and for use in mobile laboratories.

2) It is fast (2 minutes), enabling the operator to take corrective action quickly.

3) It may be correlated with the standard COD values in a large number of instances.

4) It is applicable over a wide range of COD concentrations (10-300 mg/l) and may, of course, be used outside of this range by appropriate dilution.

3.2.2.4 Limitations of the CO_2D Method

A. Stenger and Van Hall (Ref. 27) reported that the CO_2 oxidations were only linear for standard solutions containing more than 100 mg/l, and that their results closely paralleled those obtained with the standard COD methods, the chief differences stemming from a divergence of characteristics displayed by nitrogen-containing compounds in the two systems. Thus, carbon dioxide is reduced at high temperatures by NH_3 and urea (NH_2CONH_2), but these compounds do not affect the chromic acid reagent in the standard COD procedure. Ammonium chloride (NH_4Cl) yielded anomalously high results in this (CO_2D) method, possibly because of some intermediate reaction of the HCl formed, reducing the CO_2 to CO and forming a transient platinum halide. Stenger and Van Hall (Ref. 25) suggested either measuring chloride separately and making a correction, or "spiking" standards with known amounts of chloride.

B. At high temperatures, nitrates, phosphates and sulfates release O_2 which in turn reoxidize CO to CO_2. Sulfate may be removed prior to sample injection. Nitrates are the chief offenders, but the authors noted that they would yield available oxygen in BOD tests and therefore "should not be regarded as interfering if actually a valid part of the sample." (*Loc. cit.*, p. 210). However, Helms (Ref. 28) considers this positive interference by oxygen-containing anions common in wastewater a disadvantage, and states that the methods used to compensate for the interference produce unacceptable side effects.

3.2.3 Total Oxygen Demand

Another instrument based on a dry combustion process, which correlates oxygen demand with organic content, employs catalytic burning of the sample (Pt catalyst) in a carefully controlled mixture of N_2 and O_2 (see Fig. 10) (Refs. 29, 30). Oxygen depletion is detected by means of a fuel cell (Pb-Pt) and *TOD (Total Oxygen Demand)* is recorded as a change in cell current. The change in fuel cell current output is a function of the oxygen concentration in the N_2 stream, and this depends linearly on TOD. Sensitivity of the method is ca. 10 mg/l (ppm). A solution of potassium acid phthalate, $KHC_8H_4O_4$, is used for calibration of the system. The correlation between TOD and COD for two systems is shown in Figures 11 and 12.

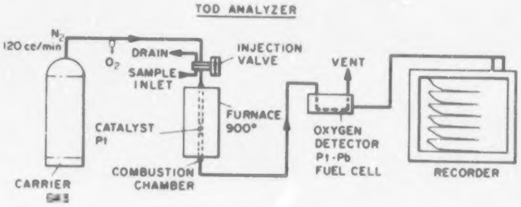

Figure 10. Schematic diagram of the TOD Analyzer (from Ref. 30).

Another version of the TOD analyzer (EnviroControl) has a fluidized bed type reactor with fine aluminum particles furnishing greatly increased surface area to promote the oxidation of carbon compounds. Here combustion occurs at 850°C, the products of combustion are cooled to 30°C and the condensed water vapor removed. Noncondensibles then enter a chamber where an oxygen sensor measures remaining oxygen. This system features a high sample flow rate of 3-4 ml/min and can handle solid particulates of diameters $\leq 100\ \mu$. Throughput per sample is about 8 minutes. TOD values are expressed in mg/l.

TOD overcomes some of the difficulties encountered in the standard COD test such as the variation in sample susceptibility to dichromate oxidation (Ref. 1). In addition, inorganic carbonates are not included as organic carbon using this method. However, nitrates decompose to give nitric oxide (NO) and O_2, and would thus reduce the apparent OD of the sample.

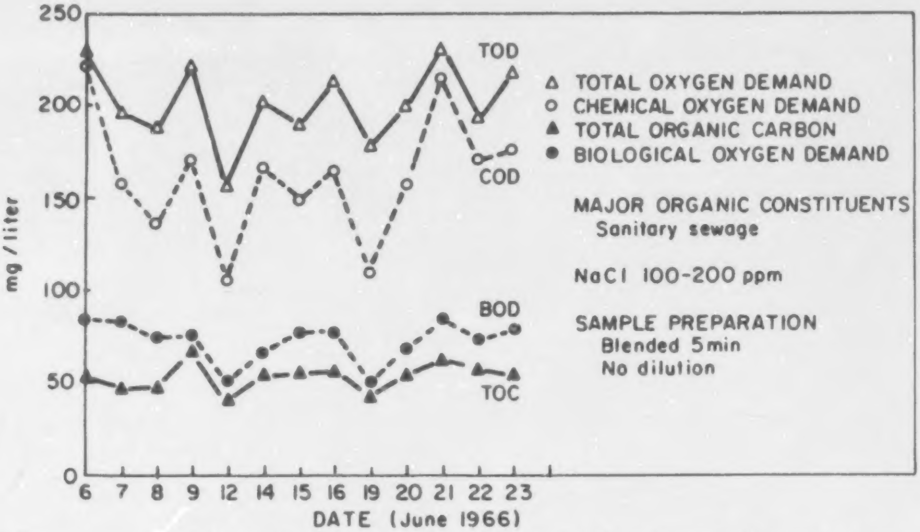

Figure 11. Comparison of TOD with COD, BOD and TOC in primary effluent (Ref. 29).

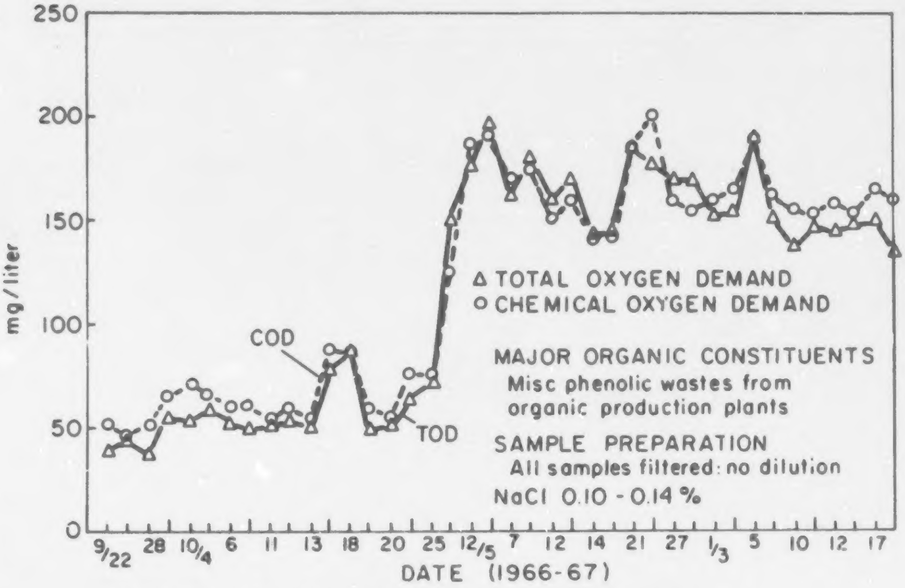

Figure 12. Phenolic treatment plant effluent (Ref. 29).

3.2.3.1 TOD Method

A typical water analysis entails the simultaneous introduction of a 20 µl sample and a stream of an inert gas into the combustion tube of an electric furnace maintained at 900°C. The carrier gas contains ca. 200 ppm of oxygen. Two reactions occur at the surface of the Pt catalyst:

1) sample impurities are oxidized by adsorbed oxygen at the catalyst surface, thereby momentarily depleting the Pt surface of its adsorbed oxygen;

2) oxygen equilibrium is restored on the catalyst surface by replacement of its depleted O_2 furnished by the carrier gas. This temporarily lowers the concentration of O_2 present in the inert gas stream.

It is this momentary O_2 depletion which is accurately measured by the lead-silver fuel cell and recorded as cell current which is thus a function of the oxygen demand of the sample. In practice the peak height measured for the unknown is compared with a standard calibration curve.

3.2.3.2 Applications and Limitations

The TOD method measures oxygen consumed in the following reactions:

$$C + O_2 \rightarrow CO_2 \qquad \text{(Eq. 3a)}$$

$$H_2 + 1/2\ O_2 \rightarrow H_2O \qquad \text{(Eq. 3b)}$$

$$N_{\text{(reduced forms)}} + 1/2\ O_2 \rightarrow NO \qquad \text{(Eq. 3c)}$$

N_2 carrier gas does not react and the lower oxidized states of sulfur form a fixed ratio of an SO_2-SO_3 mixture under TOD conditions. The oxidation of urea, for example, may be represented by the following equation:

$$2\ NH_2CONH_2 + 5O_2 \rightarrow 2CO_2 + 4NO + 4H_2O \qquad \text{(Eq. 4)}$$

Correlation of TOD with COD is good where the latter measurement does not suffer from interference (Ref. 31).

Because of greater catalytic oxidation efficiencies of the method, TOD values are normally higher than their COD counterparts, particularly on mixed or nitrogenous wastes (Ref. 32). Correlation with BOD will, of course, vary with the sample, since there is often little relationship between *biochemical* OD processes and *catalytic* oxidations at high temperature. Further, unless sample has been purged of dissolved oxygen, the TOD value obtained will represent that OD which is *in excess* of the DO present in solution.

Heavy metals may poison the Pt catalyst. This problem was taken into consideration by providing a large area of catalyst in the combustion chamber (Ref. 32).

Common anions found in natural and wastewaters do not interfere seriously, as shown in Table 3 below, where 1000 ppm of the anions in question were added to 200 ppm of organic standard in de-ionized water (Ref. 32). The presence of nitrates would, however, interfere for reasons already discussed in section 3.2.3.

3.2.3.3 Summary

Table 4 summarizes the salient characteristics of some automated oxygen demand type systems. TOD analyzers have been used to measure organics in a variety of plant and municipal effluents (Refs. 29, 32) and a number of comparisons with BOD, COD, and TOC made (Fig. 11).

Table 3.

Effect of Common Anions on 200 PPM TOD Standard (Ref. 32)

Anion Source	1000 PPM of Anion	PPM TOD Calculated	PPM TOD Found	No. Detn.	Rel. Std. Deviation
NaCl	Cl^-	200	198.2	4	± 1.41%
$NaHCO_3$	HCO_3^-	200	204.5	4	± 2.28%
K_2SO_4	$SO_4^=$	200	191.4	4	± 0.79%
$KHSO_4$	HSO_4^-	200	196.8	4	± 1.43%
Na_2HPO_4	$HPO_4^=$	200	195.2	4	± 1.54%

Table 4.

Summary of Oxygen Demand and Carbonaceous Analyzers (adapted from Ref. 33).

Parameter	Sample Treatment	Instrumental Detection		Sample Size, µl	Anal. time, min	Range	Sensitivity, ppm	Continuous Automated Operation	Requirements	Supplier
		Species	Sensor							
COD										
Standard COD	Chromate oxidation	Cr^{3+}	Colorimeter	Variable	6[a]	0-55,000 ppm of O_2	1	Yes	Reagents	Technicon
TOD Analyzer	Catalytic combustion	O_2	Fuel cell	20	3	0-1000 ppm of O_2	10	Yes	N_2, air	Ionics
AquaRator CO_2D	Catalytic combustion	CO	Infrared	20	2	10-300[b] ppm of O_2	10	Not Claimed	CO_2	Precision Scientific
TOC[d]										
Automated Analyzer	Catalytic combustion	CO_2	Infrared	(500 ml/min, 5 ml/min)[c]		25-400 mg/liter C	10	Yes	N_2, O_2, HCl (conc.)	Raytheon/AES
TOC Analyzer	Catalytic combustion	CO_2	Infrared	20-200	2-4	0-10 0-4000 mg/liter C	> 10	Not Claimed	Air or CO_2	Beckman
Total Carbon Analyzer[d]	Catalytic combustion	CO_2	Infrared	40	3	0-100 0-5000 mg/liter C	5	Yes	N_2, air	Ionics[f]
Organic Analyzer	Pyrolysis	Organic pyrolyzate	Flame ionization detector	to 50	2[e]	0-3000 mg/liter C	> 1	Not Claimed	N_2, H_2	Envirotech

[a] At a rate of 10 samples/hr.

[b] Higher concentration by dilution.

[c] 500 ml/min nominal flow rate to sample and a fraction taken for treatment at 5 ml/min.

[d] All analyzers except total carbon analyzer distinguish between organic and inorganic carbon.

[e] 6 min between analyses.

[f] formerly Union Carbide

3.3 Vapor Phase Pyrolysis

Pyrolytic fragmentation of organic compounds in the presence of water is the basis of still another total carbon analysis in an instrument marketed by Rocketdyne. A hydrogen flame ionization detector is used in the detection of the fragments produced. Dissolved CO_2 and inorganic carbonates do not interfere (Ref. 17).

Lyzyj et al. (Ref. 34) used the following procedure: The aqueous sample was introduced into the system which consisted of (1) a pyrolysis chamber maintained at 800°C; (2) a flow stabilizer column of glass beads; and (3) a detector (FID). The carrier gas was steam. An ion current signal produced by the pyrolyzed hydrocarbon fragments was detected by the FID and integrated. Glucose-glutamic acid was used as the primary calibration standard.

The method has been used to calculate the BOD values for sewage systems based on the prior establishment of ratios between the BOD measurements and the instrument response obtained for the systems examined.

Another pyrolytic system (Ref. 35), somewhat similar to the one previously described, utilizes prior conversion of the organics to methane (CH_4) in a nickel tube heated to 800°C. The carrier gas is N_2 in this instance.

The methane formed is passed through a column (H = 10 ft.) at 50°C packed with 50-80 mesh porous glass.

Methane equivalents obtained for industrial wastes using this method were consistantly higher than methane/organic equivalents obtained for natural streams.

3.3.1 Limitations of Vapor Phase Pyrolysis

The FID measures carbon concentration in terms of electric current generated (i.e., the number of ions formed). It apparently responds to all organics with the exception of formic acid (HCOOH) (Ref. 36), the response being greatest with the hydrocarbons, and diminishing as the substitution of hetero-elements increases. Properly operated, the method yields highly accurate analysis of trace levels of carbonaceous materials. However, for the routine monitoring of wastewaters, the carbonaceous analyzers of Van Hall et al. are preferred.

3.4 Summary and Evaluation of Carbonaceous Analyzers

1. With one exception, all of the vapor phase carbonaceous analyzers operate on the same basic principle: namely, oxidation of carbonaceous material and detection of the products by IR. The instruments may be calibrated in terms of carbon content or OD (BOD or COD). In the absence of systematic error(s), the form of the standard calibration has essentially no effect on the precision or the accuracy of the results obtained (Ref. 28).

2. There is no universal correlation between carbonaceous content and OD. However, for a given kind of waste, with predictable composition, the carbonaceous content bears a relationship to BOD and/or COD values, and thus can be expressed in these familiar terms.

3. Removal of interfering inorganic carbonate is effected preferably by sample precipitation of the carbonate with $Ba(OH)_2$. The two-furnace system has disadvantages associated with possible additive errors.

4. The CO_2D instrument of Van Hall and Stenger can be classified as a carbonaceous analyzer performing the function of the single furnace adaptation of the TOC analyzer. The change in oxidant from O_2 to CO_2 does not impose any fundamental furnace-design differences: it merely requires that a change in CO content be detected instead of CO_2. The basic calibration remains mg/l, although the instrument was originally calibrated in terms of COD (Ref. 25). These anions which yield oxygen on decomposition interfere significantly in the CO_2D analysis, and the suggested methods of correction have unacceptable side effects in that oxygen production from them may vary with the sample, making the correction unreliable (Ref. 28).

5. The pyrolytic method employing FID to measure trace levels of carbonaceous materials can yield very accurate data under carefully controlled conditions. However, the simple furnace carbon analyzer is more suited to the routine monitoring of waste waters. The FID response is reported to be greatest with hydrocarbons and occurs with all organic compounds except formic acid (HCOOH). Groups I and II elements are also ionized by a hydrogen flame and will interfere.

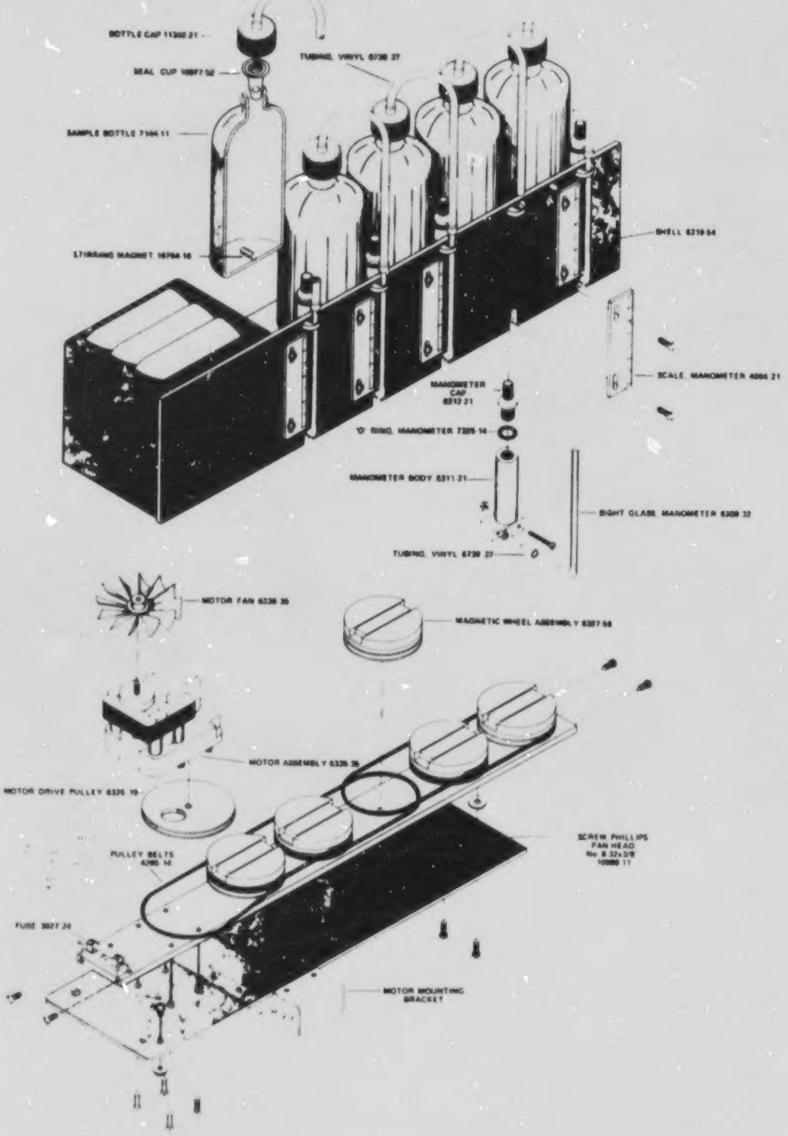
BOTTLE CAP 11300 21
SEAL CUP 10977 52
TUBING, VINYL 6730 27
SAMPLE BOTTLE 7144 11
STIRRING MAGNET 16794 16
SHELL 6319 64
SCALE, MANOMETER 4084 21
MANOMETER CAP 6312 21
'O' RING, MANOMETER 7225 14
MANOMETER BODY 6311 21
SIGHT GLASS, MANOMETER 6309 32
TUBING, VINYL 6730 27
MOTOR FAN 6330 35
MAGNETIC WHEEL ASSEMBLY 6327 64
MOTOR ASSEMBLY 6335 35
MOTOR DRIVE PULLEY 6326 10
SCREW PHILLIPS PAN HEAD No 8 32x3/8 10986 11
PULLEY BELTS 4295 14
FUSE 3027 24
MOTOR MOUNTING BRACKET

Figure 13. Assembly diagram of the Hach Model 2173, BOD respirometer (Ref. 40).

4. Biochemical Oxygen Demand (BOD): Respirometric Methods

A number of attempts have been made to automate BOD, using respirometric methods (Refs. 37, 38, 39). The respirometer measures oxygen uptake and/or gas exchange associated with some biological processes. In practice, oxygen uptake is usually measured by means of a manometer in a closed system, and the CO_2 produced in the reaction is absorbed by an appropriate reagent. The Hach Model 2173, BOD respirometer is typical of this kind of device (see Fig. 13 preceding). The measured sample is placed in a brown bottle fitted with a mercury (Hg) manometer. As the air above the sample is depleted of its oxygen by bacterial activity the pressure drop is registered by the manometer. Carbon dioxide produced is absorbed by a 45% potassium hydroxide solution placed in the seal cap. During the test period the sample is continuously agitated by means of a magnetic stirring bar activated by a pulley system connected to a motor. Clark (Ref. 41) has developed an electrolytic respirometer which generates O_2 electrolytically in response to the change in pressure which occurs during oxygen uptake. When the O_2 pressure is equal to $P_{atmospheric}$, electrolysis ceases, and the current used is a measure of oxygen uptake. The E/BOD Respirometer (Oceanography International) is based on the above principle (see Fig. 14 below).

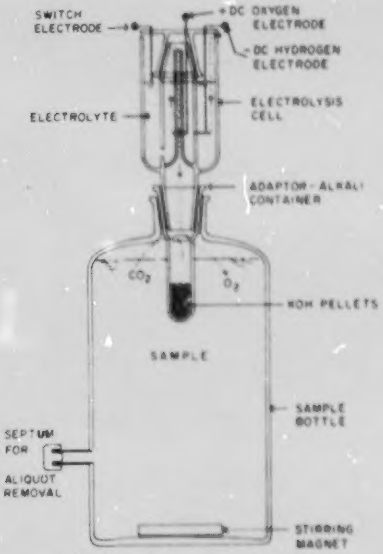

Figure 14. Schematic diagram showing the basic operation of the electrolysis system for measuring BOD (Ref. 42).

Liebmann and Offhaus (Ref. 43), using a similar technique (the Sapromat A6 Respirometer) reported obtaining oxygen uptake with 5% precision. The time advantage of obtaining BOD data using such respirometric methods (48 to 72 hours) is obvious.

Another respirometric system bubbles gaseous oxygen through the sample and the disappearance of oxygen is measured by means of an oil manometer (Ref. 44). Arthur and Hursta (Ref. 45) have correlated the 4- and 7-hour O_2 uptakes with 5-day BOD. Eye, Ritchie and others (Refs. 46, 47) have used membrane electrodes to measure changes in [DO] as an OD indicator. One such device is an ordinary BOD bottle fitted with a polarographic membrane and stirrer for continuous monitoring of DO. Good data correlation was reported when this system was compared with the usual BOD method (Refs. 45, 46).

Lamb and coworkers (Ref. 48) employed a respiration cell equipped with the galvanic cell oxygen analyzer of Mancy and Westgarth (Ref. 49) and magnetic stirring, in a study of the biological treatment of industrial wastes (Fig. 15). This led to the subsequent development of a short term (STOD) test for BOD (Lamb et al., Ref. 48).

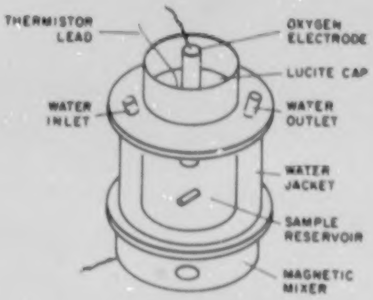

Figure 15. Respiration cell (Ref. 48).

5. Miscellaneous Monitoring Methods: Bio Parameters

Attempts have been made to correlate a number of physical parameters with the oxygen demand characteristics of biosystems. Among these, temperature plays a vital role which has been discussed (see BOD section 2.1 Temperature; DO section 1.2 Temperature Effects). Temperature measurement is discussed under Physical Parameters in this volume and will therefore not be considered in this section.

Similarly, factors such as pH and salinity affect DO and BOD (see H2O:DO, 1.3 Electrolyte Effects; H2O:BOD, 2.5 Nutrients). Again, description of these physical parameters and their measurements appear elsewhere (this volume, PHY), and so will be omitted from this chapter.

In the following section we will describe the use of *oxidation-reduction potential (ORP)* as a biometric tool in evaluating the state of aqua-systems.

5.1 Oxidation-Reduction Potential (ORP) in the Monitoring of BIO Systems

Biological systems are complex and dynamic in nature, and the biochemical changes occurring within them are frequently of a thermodynamically reversible kind. Their reactions are strongly environment-dependent, with *oxygen-reduction potential (ORP)*, hydrogen ion concentration (pH), and temperature ranking as the three most fundamental environmental variables or parameters. Measurement of ORP provides an over-all system potential, which embraces many interrelated reactions and phenomena, not all of them amenable to individual measurement. By the indication of the redox state of an aqua-system one can obtain an insight into the biological condition of that system (Refs. 50, 51, 52). For in-depth discussions of ORP theory as it applies to biological systems, the reader is referred to the works of Clark (Ref. 53) and Barron (Ref. 54).

5.1.1 Theory of ORP

The *electrochemical potential* of a system is associated with its *driving force* or tendency to lose or gain electrons. At equilibrium the free energies of products and reactants will be equal and the system potential depends solely on the concentration of the reactant and product species remaining. Using the standard hydrogen electrode* as a reference for potential measurement, the reduction potential for a system

$$M^{b+} + (b - a)e \rightleftarrows M^{a+} \qquad \text{(Eq. 5)}$$

where $b > a$, may be written as the Nernst expression:

$$E_{M^{b+}M^{a+}} = E^0_{M^{b+}M^{a+}} - \frac{RT}{(b - a)F} \log \frac{a_{M^{a+}}}{a_{M^{b+}}} \qquad \text{(Eq. 6)}$$

where:

E^0 = the standard reduction potential for the system, i.e., (for $a_{M^{b+}} = a_{M^{a+}} = 1$) compared with the standard hydrogen electrode,
$(b - a)$ = the number of electrons transferred,
R = the gas constant,
T = absolute temperature, and
F = the Faraday, in appropriate units.

To measure $E_{M^{b+}M^{a+}}$ for the half cell reaction of the system, the following cell assembly is employed:

$$\text{Pt}|\text{H}_2,\ 1\ \text{atm}|\text{H}_3\text{O}^+,\ a = 1||M^{b+},\ M^{a+}|\text{Pt} \qquad \text{(A)}$$

The following half cell reactions occur in this cell assembly:

Anode: $\frac{1}{2}H_2 \rightleftarrows H^+ + e,\ E^0_{H_2} = 0.000\ V$ (Eq. 7)

Cathode: $M^{b+} + (b - a)e \rightleftarrows M^{a+},\ E^0_{M^{b+}M^{a+}}$ (Eq. 8)

For a system using the standard electrode ($E^0_{H_2} = 0$) both the magnitude and sign of the overall cell potential are identical with its ORP. The sign will of course depend on the sign of the E^0 term in Eq. 6 and the relative concentrations of the charged species in question.

For the cell system (A) shown, the ORP will be negative if the electrons flow from the H electrode to Pt, $M^{b+}M^{a+}$ and the reaction of Equation 6 will then go spontaneously. For the case of opposite electron flow (i.e., to the H electrode), the following equations (i.e., half cell reactions) maintain:

Anode: $M^{a+} \rightleftarrows M^{b+} + (b - a)e$ (Eq. 9)

Cathode: $H^+ \rightleftarrows \frac{1}{2}H^0_2 - e$ (Eq. 10)

Here the ORP will be positive.

Since the convention used is based on the standard hydrogen electrode, the notations ORP and E are used interchangeably.

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*The standard hydrogen electrode is assigned zero potential for $a_{H^+} = 1$, $p_{H_2} = 1$ (at 25° C). (a = activity; p = pressure in atmospheres)

Still another expression for the ORP parameter is in terms of pE. This is analogous to the expression for pH and takes the form

$$pE = pE^{\circ} + \frac{1}{(b - a)} \log \frac{M^{b+}}{M^{a+}} \qquad \text{(Eq. 11)}$$

Here,

$$pE = \frac{E_{M^{b+}M^{a+}}F}{RT} \quad \text{and} \qquad \text{(Eq. 12)}$$

$$pE^{\circ} = \frac{E^{\circ}_{M^{b+}M^{a+}}F}{RT} \qquad \text{(Eq. 13)}$$

pE is a measure of equilibrium *redox intensity*, where a large positive value is indicative of a strongly oxidizing condition in an aqua-system. Conversely, a low positive--or negative--pE indicates reducing conditions. For water solutions the pE range is -10 to +14.

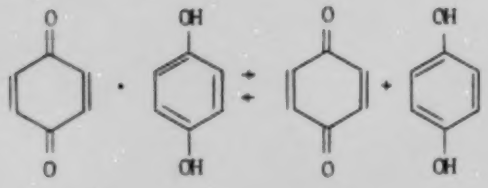
Since the standard H electrode is not a convenient reference electrode, other electrodes are generally employed, one of the most widely used being the *calomel electrode*. For 1 molar KCl ($a_{Cl^-} = 1$), $E^{\circ}_{calomel} = +0.268$ V. Expressed in terms of the standard hydrogen electrode,

$$E_H = E_C + 0.268 \text{ V} , \qquad \text{(Eq. 14)}$$

where:

E_H = the ORP value of the system using a H reference electrode,
E_C = the ORP value in terms of the calomel reference electrode, and
0.268 V = the standard reduction potential for the calomel reference electrode (1 M KCl).

Quinhydrone may be used to standardize the ORP cell by allowing the indicator electrode (Au or Pt) to come in contact with a saturated quinhydrone solution. This is a simple technique, depending on the rapid dissociation reaction of the molecular compound to quinone (Q) and hydroquinine (HQ):



(QH) (Q) (H)

(Eq. 15)

A potential develops rapidly, and the QH electrode is relatively resistant to poisoning. However, standardization must be carried out between pH 1-8 (Ref. 33, p. 1482).

5.1.2 ORP Measurement

Measurements of ORP are made with an electrode pair consisting of a noble metal non-polarizing indicator electrode and a reference electrode, such as Ag-AgCl or the calomel electrode (Hg-Hg_2Cl_2). The indicator electrode to which electrons are transferred by the redox system may be in the form of a button or wire. Measurement of the emf developed may be by means of a potentiometer or voltmeter (Fig. 16c). Details of the procedure are given in Ref. 24b. (ASTM Standard test D1498-59). Depending on the accuracy required, one of three types of meters may be used. Table 5 gives electrical characteristics for three assemblies.

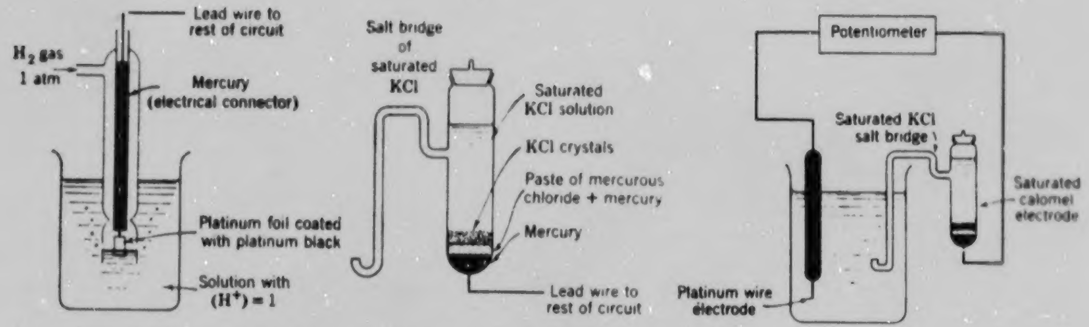
The ASTM method employs a saturated calomel reference electrode with an excess of solid KCl and of calomel surrounding the pure Hg component. It requires that a fresh junction be formed between the saturated KCl solution of the reference electrode and each new test solution. The a.c. resistance at the junction may not exceed 5000 Ω, and the area of the noble metal in contact with the test solution should be approximately 1 sq. cm.

Sampling procedures are those described in H2O-DO-2.1 and HSO-BOD-12.4, or ASTM method D-510.

Calibration will depend on the type of meter employed (see D 1498-59.9).

New metal electrodes are cleaned with aqua regia warmed to 70°C for 1 minute. Since this treatment attacks the noble metal as well as removing impurities, the time specified must be closely observed. This same treatment may be applied with caution to an aged electrode whose performance has become unreliable.

Just prior to use the electrode is cleaned with (1:1) HNO_3 by gradually warming to boiling, maintaining just below the boiling point for five minutes, then allowing the assembly to cool. The electrode is then washed repeatedly with distilled water before immersion in the sample solution. The voltage is read after the cell has reached thermal equilibrium. Readings using different oxidation-reduction electrodes should agree within ± 5 mV.


Lead wire to rest of circuit
H_2 gas 1 atm
Mercury (electrical connector)
Platinum foil coated with platinum black
Solution with $(H^+) = 1$
Salt bridge of saturated KCl
Saturated KCl solution
KCl crystals
Paste of mercurous chloride + mercury
Mercury
Lead wire to rest of circuit
Potentiometer
Saturated KCl salt bridge
Saturated calomel electrode
Platinum wire electrode

(a) Standard hydrogen electrode. *(b) Saturated calomel electrode.* *(c) Cell for measurement of an oxidation potential.*

Figure 16. Electrodes and cells (adapted from Ref. 55, p. 28-36).

Table 5.

Electrical Characteristics of Meters and Operating Performance of Assemblies (Ref. 24)

	Type A Meter	Type B Meter	Type C Meter
Vacuum tube operation	Yes	Yes	No
Type of measuring circuit	Potentiometric	Direct Reading	Potentiometric
Method for detection of balance point	Null indicator (galvanometer or electron-ray tube)	Direct	Galvanometer[a]
Maximum current flowing in input circuit	10^{-10} amp	10^{-10} amp	
Standard cell for calibration	Yes	Optional	Yes
Scale units	Millivolts	Millivolts	Millivolts
Minimum range	0 to ± 1100	0 to ± 1100[b]	1 to ± 1100
Maximum value of smallest ruled interval	10 mV	10 mV	10 mV
Power supply: batteries or 115 Vac	Either	Either	Batteries

[a] Minimum sensitivity equivalent to 0.0005 μA at 1 m.

[b] A double scale may be provided.

Oxidation-reduction potential for the sample (in mV) is calculated with reference to the hydrogen scale:

$$ORP = E - C \quad ,$$

where

E = emf in mV for the cell, and
C = potential of the saturated calomel electrode (also in mV), referred to hydrogen.

It is to be noted that C must be corrected for deviation from standard temperature (25°C).

Precision obtained is reported as ±5 mV with type A and C meters, ±10 mV with type B.

5.1.3 Scope and Limitations of ORP

Experimental measurement of E_H in natural waters, and interpretation of the significance of the value obtained presents serious problems (Ref. 56). Firstly, natural waters harbor a broad spectrum of substances, organic and/or inorganic, in dissolved, colloidal, or suspended states, which may affect or interfere with the ORP measurement. Secondly, the recurrent cyclical input of solar energy results in a photosynthetic cycle, and characteristically low rate for redox reactions. Thus the system is an *open* one -- i.e., does not attain equilibrium. The numerous redox systems present are furthermore not distributed homogeneously throughout the aqua-environment, so that the attainment of an overall equilibrium for the system is highly unlikely. The *open* or *dynamic* nature of the aqua-system exists both on a localized (*micro*- or molecular) and non-localized (*macroscopic* or environmental) level and the bio-systems within these natural waters may be viewed as functioning on both levels.

On the molecular level, the response of living organisms to an ORP system may be viewed in terms of the presence (or absence) of electroactive substances (*mediators*) -- i.e., trace metals, and/or the latter in combination with appropriate enzyme systems. Bacterial systems have been classified on the basis of their electroactive response (Barron). On the macro level, microorganisms function at a much more complex level, since other environmental substances present, and their interaction with metabolites, can be affected by the other physical and chemical parameters and by their own surface activity. Even given a hypothetically uniform distribution not possible under dynamic stream conditions, many redox systems would not couple in the normal course of events. Thus, although the ORP measurement is a valid one on a macro scale, it is unrealistic to assume that an ORP measurement reflects any micro (i.e., *molecular*) system.

The number and complexity of the redox systems present also contribute to the problem of interpretation of experimental measurements since an E_H value may reflect the sum of the potentials of a number of biosystems (*mixed potential*, E_m), and thus cannot possibly yield any information on individuals, even of a qualitative nature. Interaction between systems can lead to a slowly changing E_m value, and low concentrations of certain redox species can interfere with the successful measurement of E_H. Differing half cell reactions may show these effects to a varying degree. The following factors are involved:

a) exchange current i_0;

b) electrode area, A (cm^2);

c) electroactive species involved (the products of their concentrations: $C_{ox}C_{red}$ (mol cc^{-1})).

The dependence of i_0 is given in Equation 16 below:

$$i_0 = AnFK' C_{ox}^{(1-\alpha)} C_{red.}^{\alpha} \quad , \qquad \text{(Eq. 16)}$$

where

n = the number of electrons in the half cell reaction;
F = the Faraday, and
α = the transfer coefficient (usually ∿ 0.5).
K = a reaction rate constant (cm/sec).

For systems with $i_0 > 10^{-7}$ amp., E_H is a reasonably measurable quantity. By the use of electrodes with large surface areas, the low exchange currents, i_0, resulting from slow reaction rates may be measured. There are practical limitations to increased electrode areas, since they adsorb surface active pollutants, thereby suffering reduction in electroactive area.

The value of E_H is further affected by *poising capacity* -- a quantity similar to the buffering capacity in acid-base solutions. The *poising index* is defined as the "increment of oxidizing agent in equivalents/1, divided by the incremental change in E_H" (Ref. 53). Without poising capacity, potential instabilities hamper measurement. This is often a problem in muds and lake waters (*electrode poisoning*). It may also result from sample dilution with distilled water.

For solutions which have poor poise, the Pt electrode surface area is critical. In addition, an electrode may require a long adaptation period before attaining equilibrium in a given system. However, once equilibrium is achieved, the response for the system in question becomes satisfactory.

5.1.4 Summary and Conclusions

The dynamic (non-equilibrium) states of natural water systems, the multiplicity of redox couples, and the existence of numerous experimental difficulties, have all militated against the use of the ORP as a water monitoring parameter. Nevertheless ORP does have some value in defining conditions under which some algal and/or bacterial species are favored. This can be very important in sanitary engineering process control and in some environmental investigations (Ref. 50).

The eco-concept states that there is a mutual interrelationship between all parts of a bio-system. Although bio-systems are dynamic and classified as open, they are nevertheless viewed as existing in some sort of *quasi-steady state* (Ref. 33, p. 1485), other than true equilibrium, however. Lee and Hoadley (Ref. 57) found that the micro-organisms in an ecosystem, for example, figure significantly in determining the mineral content of their aquatic environment.

Hydrogen ion concentration (pH) is also an important parameter of microbial viability. Also, because of the importance of pH in the solubility relationships of enzymes, pH can effect the presence of essential nutrients in solution, thereby having a profound influence on metabolic rates and processes, not to mention the half-cell reactions.

The chief chemical species engaged in these redox reactions in the aquatic system are the metallic species Fe, Mn, and the compounds of C, N, O and S. An increase in ORP may indicate one of a number of metabolic processes, such as the oxidation of NH_3 to NO_2^- or NO_3^- (nitrification), the oxidation of sulfides to sulfites (or to $SO_4^=$) and/or photosynthetic reactions. Conversely, reductive processes such as the conversion of ferric to ferrous ion ($Fe^{+3} \rightarrow Fe^{+2}$), nitrate to nitrite ($NO_3^- \rightarrow NO^-_2$), and/or of sulfate to its lower oxidation states ($SO_4^= \rightarrow SO_3^=$, etc.), will reduce the ORP value, E_H.

Edox (oxidation) reactions furnish the energy required for bacterial syntheses in bio-systems. The *reducing* power needed for photosynthetic assimilation of CO_2, and the means of obtaining and utilizing energy in cyclic processes are provided by coupled *redox* systems.

The micro-fauna and flora of greatest significance in the ecocycles of natural waters are probably the iron-bacteria, the sulfate reducing and so-called *thio-bacteria*, and certain algae, with the photosynthetic (*green* and *purple*) bacteria, nitrifying (and de-nitrifying -- i.e., reducing) species playing relatively secondary roles. The interrelationships of these organisms are illustrated in Fig. 17 and discussed in Ref. 58.

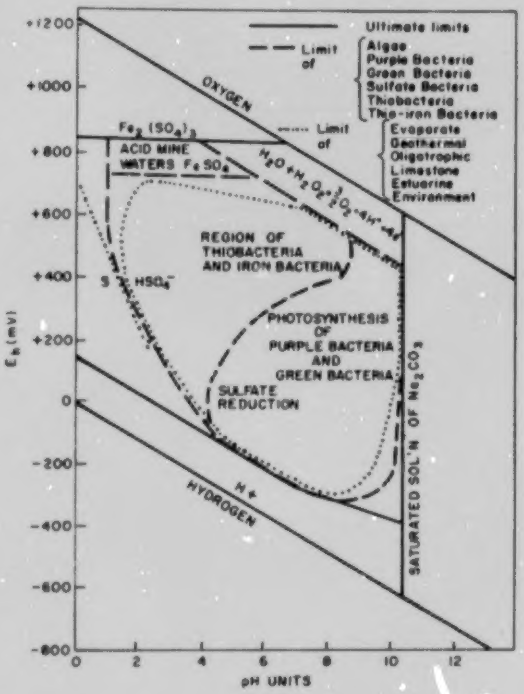


Figure 17. E_H-pH limits of the natural environments (Ref. 58).

5.1.5 Heterogeneity of Ecosystems and E_H

Measurements of different locations in an ecosystem reveal its heterogenous and dynamic aspects. E_H measurements vary with depth and with the nature of flora, lithos, etc. Fillos (Ref. 33, p. 1486) recorded variations in E_H in benthic muds. The dynamics of microbiological processes in estuarine bottom muds, as evidenced by variation in E_H, is also discussed by Wood (Ref. 58).

The reduction of $SO_4^=$ in sea water occurs at ∿-100 mV in the presence of an adequate supply of decomposed organic matter. Thereafter the E_H may be reduced to ∿ -350 mV by further reduction of $SO_4^=$ and/or extensive anaerobic digestive processes. Such a decrease in E_H may delimit the organisms which survive, favoring those groups which flourish at the lower potential. The value of E_H is believed by Wood to be influenced by respiration on the positive side and by organic reducing systems on the negative side.

Thus, by the examination of E_H data from an aquatic ecosystem some indications of existing overall environmental conditions may be obtained.

5.1.6 The Future of ORP in Waste Water Applications

The complexities of activated sludge systems limit the utility of ORP as a parameter in them. However, ORP measurements have been used as qualitative control indicators during anaerobic digestion (Ref. 54). To date, redox data have not been used strictly quantitatively in wastewater systems (Ref. 59) but rather as a means of detecting gross changes, such as the conversion from aerobic to anaerobic conditions in the system.

The aeration of wastewaters will usually result in reasonably constant E_H values above a DO content of ∿ 1 mg/l. Below this value, there is a marked decrease in E_H (see Fig. 18). Redox readings are therefore useful in monitoring anaerobic digestion processes, where they can be used to detect trends which may then be correlated with other parameters (Ref. 53). The potential value ranges for some sanitary engineering processes are shown in Fig. 18.

E_H has also been used successfully in monitoring cyanide and chromate oxidation (Ref. 60).

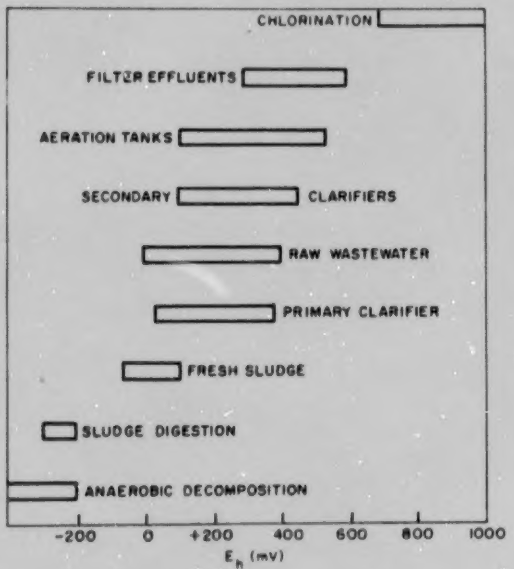


Figure 18. Potential values of some sanitary entineering processes. The E_H values are referred to the hydrogen half cell (Ref. 59).

5.1.7 Spectrophotometric Measurement of Organic Pollutants

Since many pollutants have characteristic ultraviolet (UV) absorption spectra, it is possible to use these spectra to estimate gross pollutants from industrial effluent. Bramer, Walsh, and Caruso (Ref. 61 a,b) have taken advantage of this fact in their development of a continuously monitoring UV spectrophotometer for the detection of UV-absorbers such as benzene, phenol and pyridine (10-50 μg/l). In other instances, phenolic compounds in plant effluents have been monitored by means of the bathochromic shifts* in their wavelength maxima. Similarly the composition of reaction mixtures from certain industrial processes and effluents has been determined. The latter procedure is based on the spectral characteristics of aromatics and conjugated systems (Ref. 17). Under relatively constant pollutant conditions. with such UV absorbers in effluent waters it should be possible to establish at least some rule of thumb relationships between the chemical parameters of specific absorbers and their BOD, while keeping in mind the quantitative limitations to these extrapolations.

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*bathochromic shift -- a shift to longer wavelength.

5.2 Summary: Future Trends

With the increasing demands in the management of water quality, instrumental monitoring of natural waters and industrial effluents is clearly the trend of the future. Biological parameters remain the most important indicators of water quality, but they are also the slowest to measure and the most difficult to automate. While samples collected from natural and waste waters undergo more and more sophisticated analysis, the biological methods used are often of necessity those that were in vogue more than half a century ago.

Although the crux of many current water quality investigations is biological examination, it is highly unlikely that indicator organisms, which have proven their worth as *qualitative* criteria in the monitoring of aquatic ecosystems, will soon provide us with *quantitative* data -- and it is even less likely that such methods will be readily amenable to automation. Nevertheless, it is not inconceivable that some of the control methods employed by the drug industry, for example, in the synthesis of antibiotics may ultimately be applicable to water pollution monitoring -- or for that matter, the biochemical methods developed in photosynthetic studies with radioisotope-labelled nutrients. But these are approaches of the future. For the present, identification of the biota collected in a grab sample is still a slow process and requires in addition a good deal of expertise. The number of samples which can be processed by such methods is strictly limited, as is their frequency. For this reason, there will of necessity be an increased reliance on more rapid, short term, but biologically correlated measurements. Among these, parameters such as STOD and ΔCOD, using mass culture aeration techniques and some of the more rapid respirometric methods described here and in the BOD chapter, have already shown promise and should be further developed.

Automated wet chemical methods have already proved their utility in COD and amino acid analysis, where large numbers of samples are involved. However, the dry combustion COD techniques generally have the advantage of requiring less complicated sample treatment, fewer steps, and fewer reagents.

As a rule, automated methods require a good fundamental comprehension of the chemical processes involved and the nature of the problems encountered in specific systems. They also demand a degree of technical expertise and a knowledge of electronics not usually in the arsenal of the routine analyst. Thus, these methods are best suited to larger laboratories with the economic capabilities necessary for the most effective use of these tools, as well as their continuous maintenance in good working order.

Biochemical redox systems such as DPN* and TPN* employing reactions such as the TPTZ-ATP* test also deserve further scrutiny. For a more detailed discussion of automated enzymatic analyses and the use of bio-activators and inhibitors, see Ciaccio et al., Vol. 4 in Ref. 33, Chapter 27, pp. 1515-1523. Finally, the wealth of expertise developed in the antibiotics industry and in photosynthesis studies may well furnish us with some valuable approaches in the future.

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*DPN: diphosphopyridine nucleotide
*TPN: triphosphopyridine nucleotide
*TPTZ-ATP: triphenyltetrazolium chloride -- adenosine triphosphate.

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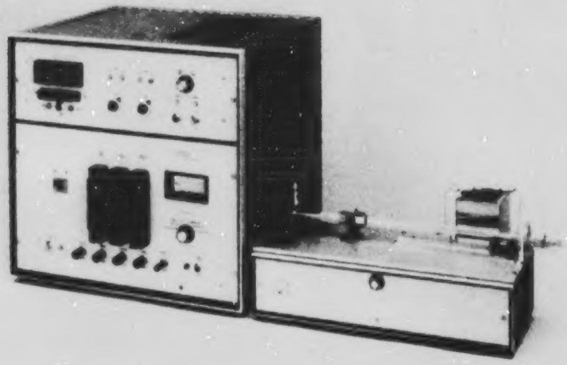
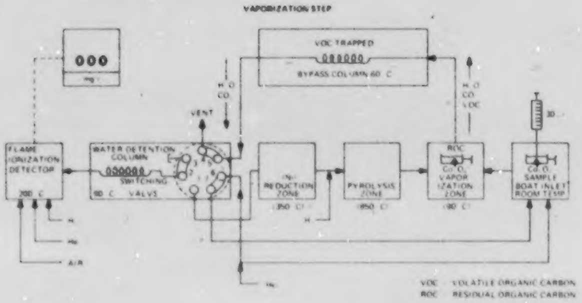
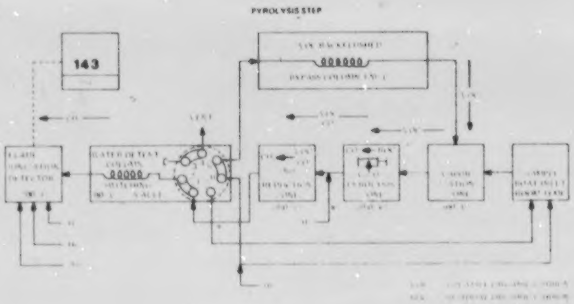
H20-BIO
Field: TOC
Dohrmann 1
June 1975

Total Organic Carbon Analyzer

Dohrmann Model DC-50




VAPORIZATION STEP
000
VOC TRAPPED
BYPASS COLUMN 60 C
H O
CO
VENT
H O
CO
VOC
30
FLAME IONIZATION DETECTOR
200 C
WATER DETENTION COLUMN
SWITCHING
90 C VALVE
REDUCTION ZONE
(350 C)
PYROLYSIS ZONE
(850 C)
ROC
VAPORIZATION ZONE
(90 C)
SAMPLE BOAT INLET ROOM TEMP
H
AIR
VOC - VOLATILE ORGANIC CARBON
ROC - RESIDUAL ORGANIC CARBON


PYROLYSIS STEP
143
VENT

Class	Laboratory/portable
Categories of Water	Fresh/Saline/Waste
Principle of Operation	Catalytic reduction of carbon allows materials to methane which is measured by flame ionization detection (FID)
Sensitivity	1 ppm
Range	1 to 2000 ppm; (± 1 ppm ± 2%)
Interferences	Appreciable interferences from: no specific interference Moderate interferences from: Slight or no interferences from:

Multi-Parameter Capability

Also determines total carbon (organic + inorganic) and inorganic carbon (by difference, i.e., TC - TOC)

Sampling

Method: Batch, via calibrated syringe
Volume: 30 ul homogeneous water sample (acidified)
Collection efficiency: At least 99% with homogeneous sample
Sampling module: An inert (Pt) boat charged with oxidant. An interchangeable ball joint connector provides rapid sampler-analyzer couplings.

Performance

Accuracy:
Reproducibility: ±1mg/l or 2% whichever is greater
Linearity: Equal or better than reproducibility
Analysis time: 5 min/sample
Drift: Zero drift correction

Operation

Over-all temperature characteristics:
Spec: 4.5-35° C (40-95° F)
Relative humidity: to 95%
Sample processing: Multi-step, operator attended
Calibration: Operator-performed using standard solution
Procedure: For TOC a 30 ul acidified water sample is injected into a sample boat containing a cobalt oxide oxidizer at R.T. The boat is advanced to the 90° C vaporization zone whence H20, CO_2 and volatile organics (VOC) are swept into the bypass column. Here VOC is trapped on a Porapak Q column maintained at 60° C, while H20 and CO_2 are swept through the switching valve and vented to the atmosphere.

After sample vaporization, the valve is automatically switched to the pyrolyzer position and the boat advanced to the pyrolysis zone. Residual organics (ROC) react with the catalyst at 850° C, producing CO_2. The bypass column is simultaneously backflushed at 120° C, sweeping VOC through the pyrolysis zone. Both VOC and CO_2 from the ROC are swept by HO into the H_2-enriched reduction zone over the Ni catalyst. Here all the carbon is converted to CH_4 at 350 ° C.

The reduction product is swept through the switching valve and water retention column into the FID which responds linearly to CH_4. The detector output is integrated and displayed on a digital meter in mg/l or ppm.

For TC, the function switch is set to TOTAL CARBON and the sample is put through the vaporization and pyrolysis steps without prior acidification. With the switching valve remaining in the pyrolyze position, all carbonaceous material is directed to the detector.

Maintenance: MnO_2 oxidant replaced daily; Ni catalyst on alumina support replaced periodically (6 mos. to 1 year estimated) depending on use. FID cap assembly, which holds all electrodes, is removable from outside the detector for maintenance.
Data display: Digital, 0 to 1999
Outputs: Digital, binary coded; analog, ca. 1 mV/10 ppm (30 µl sample)

Requirements

Power: 12 A at 115 VAC, 50/60 Hz
Water: Moderate flow via 1/4" connectors
Hydrogen: 70 cc/min (prepurified) @ 20 psig
Helium: 175 cc/min (prepurified) @ 20 psig
Air: 300 cc/min (prepurified) @ 20 psig
Size: 48.2 cm H, 73.5 cm W, 43.1 cm D (19" × 29" × 17")
Weight: 43 Kg (95 lbs) net
57.5 Kg (115 lbs) shipping

Features

Contains four temperature-controlled ovens (±0.5° C); the two furnace sections are Triac-controlled and capable of continuous operation at 1000° C. High temperature sections are water-cooled.
Detector: 3 section, stainless steel, with sapphire insulated collector electrode. Leakage $<10^{-14}$ A up to 500° C.
Reduction catalyst: Ni on activated alumina.

Output: Digital - BCD, 1248 Positive True
Analog - Approx. 1 mV per 10 mg/1 from a 30 µl sample
Training: See under Remarks
Options:

PART NO.	DESCRIPTION	PRICE
	DC-50 TOTAL ORGANIC CARBON ANALYZER	
832050	115 VAC, 50/60 Hz	$7875.00
832051	230 VAC, 50/60 Hz	7990.00
	DC-50 TOC ANALYZER WITH THE ABI-1	
832052	115 VAC, 50/60 Hz	8665.00
832053	230 VAC, 50/60 Hz	8780.00
526020	AUTOMATIC BOAT INLET	1420.00
899818	ABI Retrofit Kit (for DC-50 units with Serial Number 8269 and below)	260.00

References

a) Manufacturer's bulletin no. SM-674-072750
b) Y. Takahashi, R. T. Moore, and R. J. Joyce, "Direct Determination of Organic Carbon in Water by Reductive Pyrolysis" Am. Laboratory 4 (7), pp 31-38 (1972).

Cost

$7875.00 (Sept 1974)

Remarks

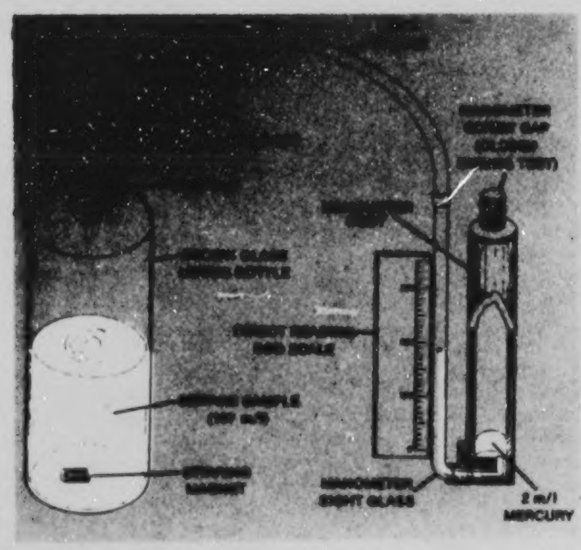
Analyzer price includes start-up assistance and operator training.
Manufacturer claims the following useful features:

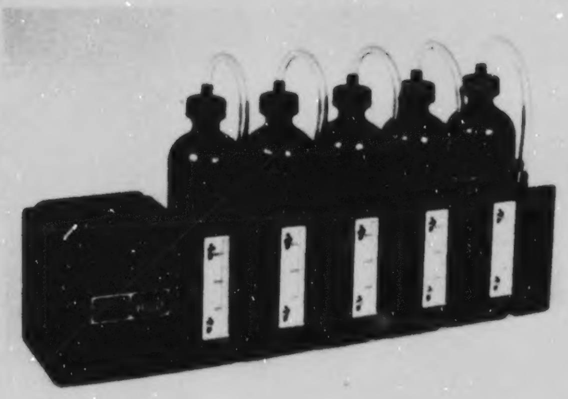
1) Freedom from sample handling in cases of high salt and silt.
2) Volatile organics data can be monitored separately from Total C.

Address

Dohrmann Division
Envirotech Corporation
3240 Scott Boulevard
Santa Clara, California 95050
Attn: Robert J. Joyce, Product Manager or John McCutchen, In-House Sales Mgr.
(408) 249-6000 Cable DOHRMANN

Biochemical Oxygen Demand
Hach Model 2173 BOD Apparatus





Class	Batch
Categories of Water	Sewage/wastewater
Principle of Operation	A measured sample of sewage or wastewater is placed in one of the bottles (Step 1) and connected to a closed-end Hg manometer. Above the sample is air containing 21% oxygen. Bacteria present in the sample utilize dissolved oxygen for their oxidation of organic matter, thereby depleting the sample of its oxygen. The deficient oxygen is replaced by dissolution of oxygen from the supernatant air, resulting in an air pressure drop over the liquid. This registers on the manometer whence it may be read directly as mg/l BOD.
Minimum Detectable Sensitivity	∿2 mg/l on 0-30 range; ∿20 mg/l on expanded scale
Range	May be selected by varying sample volumes: from 0-35 mg/l to 0-350 mg/l BOD
Interferences	Toxic metals, extremes of pH: sample is buffered to pH 7.2 (optional pH range, 6.5-7.5)
Multiparameter Capability	N/A
Sampling	Method: Batch Volume: 157 ml sample in 1 pt. reaction bottle Maximum Temperature Input: 20°C or 35°C Collection Efficiency: N/A Maximum Number of Sample Sources: 5

Performance	Accuracy: ±5% Reproducibility: Linearity: Noise: Lag Time: N/A Rise Time: N/A Retention Time: N/A Fall Time: N/A Zero Drift: N/A Span Drift: N/A
Operation	Ambient Temperature Range: 20°C ±1° (18°F) maintained during test, either in an incubator or by use of a refrigerator unit converted with a Hack "Incutrol/2" conversion unit. Temperature Compensation: N/A Relative Humidity Range: up to 100% Calibration: Calibrated against standard glucose solution Procedure: After the system containing the sewage or wastewater sample is sealed, it is agitated continually during the test period (usually 5 days) by means of a magnetic stirrer. The stirrer is rotated via a pulley system connected to an external motor. The CO_2 formed during the metabolic process is removed by absorption in 45% KOH solution placed in a seal cup in the neck of the bottle. The procedure consists of the following steps: 1) a measured sample is added to the bottle; 2) the magnetic stirring bar and seal cup containing KOH are inserted; 3) the bottle is capped lightly and stirring begun; 4) when temperature equilibrium is attained, manometer and bottle caps are tightened to seal the system; 5) the direct reading scale is zeroed and the test begun. Unattended Period: Maintenance: Minimal: designed sturdily, with few moving parts. Manufacturer predicts many years of trouble-free operation
Requirements	Power: 115 Vac, ~60 W; Incutrol/2: Heating element, 300 W max Fan, ca. 30 W (continuous load) Weight: Shipping wt, 6.8 kg (15 lb); Incutrol: 3.18 kg (7 lbs) Dimensions: 5.25 x 27.9 x 11.1 cm
Features	Output: Direct reading manometer calibrated in mg/l Training: Minimal Options: Model 2173 Hach BOD Apparatus; 230 V/59 Hz $250. Model 2597 Incutrol, 115V or 220 V $165.
References	Hach Brochure, "For Wastewater...Simplified BOD Test H. Raymond Tool, "Manometric Measurement of the Biochemical Oxygen Demand," Water and Sewage Works, 114 (6) 211 (1967) (Repr. 18 pp) P.L. D'Alessandro & W.G. Characklis, Water and Sewage Works, 119 (9), 106 (1972) (Repr. 2 pp)
Cost	Hach Model 2173 BOD apparatus, complete $250. Includes: rack, 5 sample bottles, mercury, seal caps, magnetic stirring bars and all required fittings
Remarks	BOD samples incubated at 35°C for 2-1/2 days give analyses comparable with those obtained in the standard (20°C) 5-day BOD test.
Address	Main Office: Hach Chemical Co. P.O. Box 907 Ames, IA 50010 (515) 232-2533 Attn: General Sales West Coast Office: Hach Chemical Co. P.O. Box 477 Laguna Beach, CA (714) 494-7421 Attn: Grant Wetzel, Manager West Coast Sales Office

Biochemical Oxygen Demand
Oceanography International, E/BOD Respirometer

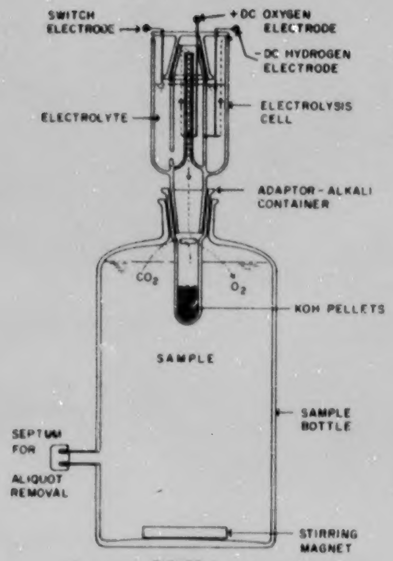
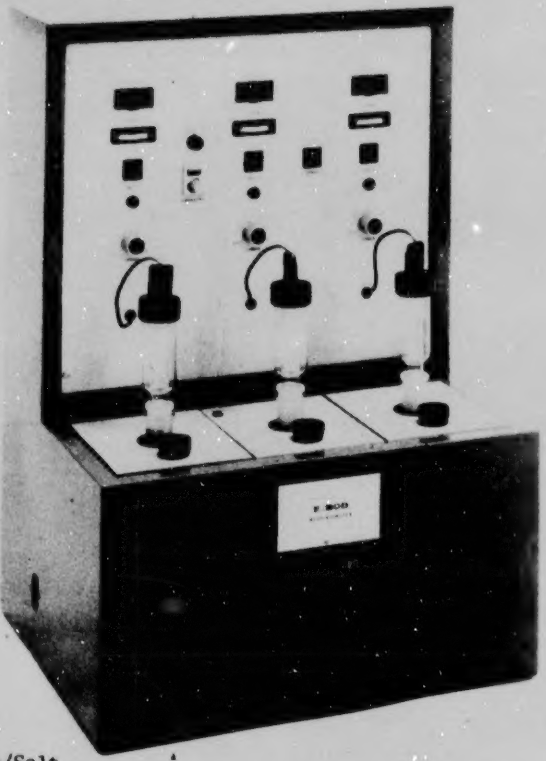

SWITCH ELECTRODE
+DC OXYGEN ELECTRODE
-DC HYDROGEN ELECTRODE
ELECTROLYTE
ELECTROLYSIS CELL
ADAPTOR - ALKALI CONTAINER
CO_2
O_2
KOH PELLETS
SAMPLE
SAMPLE BOTTLE
SEPTUM FOR ALIQUOT REMOVAL
STIRRING MAGNET

FIGURE 1

SCHEMATIC DIAGRAM SHOWING THE BASIC OPERATION OF THE ELECTROLYSIS SYSTEM FOR MEASURING BOD



Class	Batch
Categories of Water	Municipal/Industrial/Waste/Salt
Principle of Operation	Automatically measures BOD by electrolysis. The system contains a reaction chamber, an electrolysis cell, an incubator (proportionately controlled) and a measuring unit. The reaction chamber is a 1.25 l vessel provided with a top-mounted electronic oxygen generator, a stirring bar, and a manometric switch. As oxygen is used up biologically or chemically, any CO_2 produced in the process is absorbed by KOH pellets present in the vessel, producing a slight vacuum in the air space. This triggers the manometric switch and electrolytic oxygen is produced to replace the O_2 consumed. Oxygen generated by electrolysis may be related to the current applied and the time during which O_2 is being generated via Faraday's Law. The cell electrolyte employed is 2N H_2SO_4. Electrolysis (i.e., passage of direct current) results in the generation of O_2 gas at the anode and H_2 gas at the cathode.
Minimum Detectable Sensitivity	0.5 mg O_2
Range	Maximum O_2 Production: 60 mg/hr Stirrer: 50-1700 rpm Incubator: ±15°C from ambient Counter: 9999.9 mg in mg and 1/10 mg

Interferences

Changes in barometric pressure; long lag periods due to toxicity or lack of acclimated organisms. Manufacturer provides pressure correction equation and recommends the use of acclimated seed and the exclusion of toxic materials whenever feasible.

Multiparameter Capability

N/A

Sampling

Method: Discrete sample
Volume: 1 liter ±.05
Maximum Temperature Input: 35°C
Collection Efficiency: N/A
Maximum Number of Sample Sources: N/A

Performance

Accuracy: Depends on sample, within ca. 5-8% of standard methods
Reproducibility: 1-2%; sewage samples ∿4-7%
Linearity: N/A
Noise: N/A
Lag Time: 12 sec
Rise Time: 12 sec
Retention Time: N/A
Fall Time: N/A
Zero Drift: ±1 mg/5 days
Span Drift: ±1 mg/5 days

Operation

Ambient Temperature Range: 20°C or 35°C
Temperature Compensation: Incubation and temperature control at 20°C and 35°C is provided
Relative Humidity Range:
Calibration: Reference standard is a known quantity of Na_2SO_3 which reacts in the presence of $CoCl_2$ catalyst, consuming a stoichiometric amount of O_2. The reaction rate is controlled by limiting the stirring rate, which in turn limits the rate of oxygen transfer. The electrolytic O_2 generator is prepared as described in the manual, except that KOH absorption pellets are omitted. One liter of H_2O is allowed to come to temperature and D.O. equilibrium in the generator, 1 ml of $CoCl_2$ solution and 1 g Na_2SO_3 crystals are added and the generator re-sealed. O_2 is monitored for 3-4 hrs. Cumulative oxygen should attain a value of 126.4, ±2 mg O_2 and uptake should then cease. The system is allowed to run for a short time beyond the endpoint to insure complete reaction.
Procedure: A 1 liter sample is allowed to react in an air-tight chamber at constant temperature, with complete mixing. As chemical or bio-oxidation proceeds, the partial vacuum created in the reactor is compensated by the electrolytic production of O_2 in the oxygen generator to replace oxygen consumed. Cumulative oxygen demand may be read directly from counters at any time during the test period.
Unattended Period: May be run unattended "for long periods."
Maintenance: Occasional cleaning of glassware.

Requirements

Power: 115 Vac, 60 Hz single phase (220 V, 50 Hz optional)
  Instrument electronics Supply:
    Electrolysis cell: 20 Vac, 200 ma
    Incubator: 200 watts
    Magnetic Stirrer: 115 Vac, 60c, 0.5 amp
    Counter: 20 VdC
Weight: 39.5 kg (87 lbs)
Dimensions: Case: 76.2 x 55.9 x 41.9 cm (30" x 22" x 16.5")
  Glass Reaction Chamber: 27.4 cm H x 9.5 cm ID (8.8" H x 3.7" ID)
  Sample Port: 1/4" glass tubing; std 29/42 ground glass joint

Features

Output: Connector to optional printer only
Training: Operator training by factory representative optional
Options:

206EP Printout, monitors and cumulative O.D.for 15 or 60 minute intervals. Simultaneous 3-cell OD (to 0.1 mg O_2).	$1,675.
Standard Printout for 3 or 6 cells, Option to 15 cells.	
206S/B Sludge/Benthic O_2 Uptake Accessory	$ 620.
206SBT Silicone Rubber Tubing (per foot)	$ 3.07
2004K Accessory Kit	$ 33.90

Contains:
2 ea. BD 2431B, 5 ml syringe
2 ea. BD1100, 17 gauge 2" needle
2 ea. BD 1108, 15 gauge 3-1/2" needle
1 ea. 2 oz. tube stopcock grease
1 ea. packet 1/4 lb. KOH pellets
20 ea. special septums
1 ea. interstice filler bottle
1 ea. rack for electrolysis cell

Also Available:

6-206	6-Sample Capacity E/BOD Respirometer	$ 5,350.
9-206	9-Sample Capacity E/BOD Respirometer	$ 7,590.
12-206	12-Sample Capacity E/BOD Respirometer	$ 9,610.
15-206	15-Sample Capacity E/BOD Respirometer	$12,220.

References

1) Manufacturer's Brochure: "The E/BOD Respirometer System."
2) "A Proposed Standard Method Test for Oxygen Demand Determination by Electrolysis in Wastewater," 12 pp., incl. 11 refs. (typewritten booklet provided by the manufacturer.)
3) J.C. Young and J.W. Clark, "Growth of Mixed Bacterial Populations at 20°C and 35°C," *Water and Sewage Works*, 112 (7), pp 251-5 (1965).

Cost

3-Sample Capacity E/BOD Respirometer Includes stirrers, incubator and electronic counters.	$2,820.

Remarks

The reactor is provided with a septum for removal of aliquots with a syringe for the measurement of other parameters. Incubation and temperature control at 20°C and 35°C are provided (according to Young and Clark, a 2-1/2 day BOD at 35° is equivalent to the 5-day BOD at 20°C, within experimental limits).

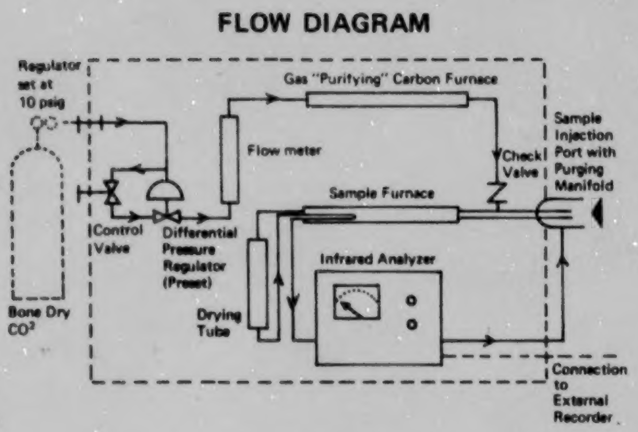
Address

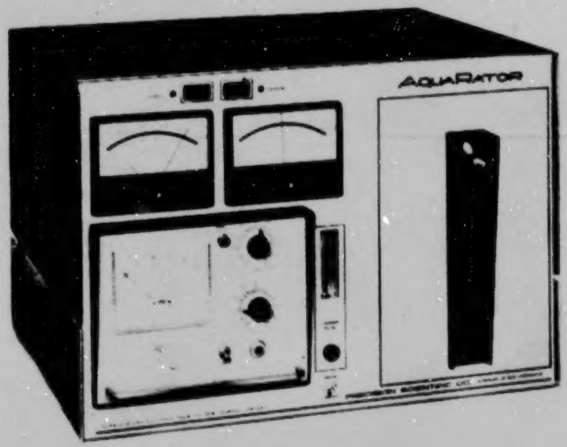
Oceanography International Corporation
512 West Loop
P.O. Box 2980
College Station, Texas
(713) 693-1711 TWX: 510 - 892 - 7944
Attn: Alan D. Fredericks, Chief Chemist and Vice President, or
Rogers M. Hall, District Sales Rep. Tel: 846-3729, or
Ms. Jane Theis, Secretary to the President

H20-BIO
Field: COD
Precision Scientific
Sept. 1975

Chemical Oxygen Demand Analyzer

Precision AquaRator


FLOW DIAGRAM
Regulator set at 10 psig
Gas "Purifying" Carbon Furnace
Sample Injection Port with Purging Manifold
Flow meter
Check Valve
Sample Furnace
Control Valve
Differential Pressure Regulator (Preset)
Infrared Analyzer
Bone Dry CO2
Drying Tube
Connection to External Recorder



Class Laboratory/mobile lab

Categories of Water Waste

Principle of Operation Combustion of an organic substance in an O_2 and CO_2 atmosphere, respectively, may be expressed by the following equations:

$$(1)\quad C_aH_bN_cO_d + (n/2)O_2 \rightarrow aCO_2 + (b/2)H_2O + (c/2)N_2$$

$$(2)\quad C_aH_bN_cO_d + mCO_2 \rightarrow (m + a)CO + (b/2)H_2O + (c/2)N_2$$

The theoretical ultimate COD of the sample is given by the exact quantity of O_2 required to effect complete oxidation of the compound to CO_2 and H_2O. Dichromate oxidation approaches this theoretical value, but the variation in sensitivity of organics to oxidation under the vigorous conditions used by the AquaRator results in values somewhat less than theoretical. Since it has been demonstrated [Stenger and VanHall, Anal. Chem. 39, 206 (1967); Moore, Kroner, and Ruchhoft, *Ibid.* 21, 953 (1949)] that the number of moles of CO formed is equivalent to OD, it is possible to relate COD directly to CO readings.

Minimum Detectable Sensitivity 10 mg/ℓ

Range 10 to 300 mg/ℓ

Interferences Nitrates, phosphates, sulfates

Multiparameter Capability None

Sampling
Method: Discrete; via microsyringe
Volume: 20 µl
Maximum Temperature Input: Not applicable
Collection Efficiency: Not applicable
Maximum Number of Sample Sources: No restriction

Performance

Accuracy: ±1% full scale
Reproducibility: ±3%
Linearity: Nearly linear
Noise: < 1% full scale
Lag Time: Approximately 50 sec
Rise Time: IR analyzer, 90% of final reading in 5 seconds
Retention Time: 2 minutes
Fall Time: Approximately 55 sec
Zero Drift: Not determined
Span Drift: Not determined

Operation

Ambient Temperature Range: Not determined
Temperature Compensation: None
Relative Humidity Range: Not determined
Calibration: Usually effected by injection of standard solutions of $NaOOCCH_3 \cdot 3H_2O$, for which OD in mg/ℓ may be calculated. A plot of OD vs. recorder output as shown on a strip chart is used to determine OD for the sample.
Procedure: A 20 μl water sample, homogenized if solids are present, is injected into the AquaRator by means of a micro-syringe. The sample is then swept through a catalytic combustion furnace (Pt cat.) by a stream of dry CO_2, oxidizing organic pollutants to CO and H_2O. Water is then removed in a drying tube and the reaction mixture subjected to a second pass catalytic oxidation. [CO] is measured by means of an NDIR analyzer sensitized for CO, and the resultant CO reading is directly converted to COD by means of the calibration chart. Gas flow (CO_2) is set at ~130 ml/min. Any oxygen impurity is removed by reduction in a carbon furnace, yielding a mixture of CO and CO_2 which provides the normal baseline of the recorder.
Unattended Period: Variable, up to 90%
Maintenance: Designed for continuous duty

Requirements

Power: 120 V, 60 Hz or 120 V, 50 Hz. Power consumption 1500 W.
Weight: 41 kg (90 lb); shipping weight 79.5 kg (175 lb)
Dimensions: 61 x 56 x 40.6 cm (24 x 22 x 16 in.)

Features

Output: 0-100 mV
Training: None
Options: Cat. No. 62971 - Stepdown Transformer 240/120 V, 50 or 60 Hz, 2000 W

References

1) V.A. Stenger and C.E. VanHall, "Rapid Method for Determination of Oxygen Demand", Anal. Chem. 39, 206 (1967).
2) Manufacturer's brochure "AquaRator"
3) Manufacturer's letter of May 1974

Cost

Cat. No. 68900 (120 V, 60 Hz)	$8250
Cat. No. 68901 (120 V, 50 Hz)	8250
Cat. No. 62971 (Stepdown Transformer)	134.40

Remarks

Standard equipment includes special sample syringe, extra charcoal, Drierite, and instruction manual.

Not included:
1) AquaRator grade CO_2, cylinder size 1A
2) Two-stage CO_2 regulator, 5-50 psig delivery pressure
3) Tygon tubing for cylinder supply line R3603, 3/16" ID, 3/32" wall
4) Potentiometric recorder, 0-100 mV range with input impedance of ≥ 5000 Ω; chart speed, 0.2"/min; pen speed 1 to 2 seconds

May be operated on 240 V with suitable transformer.

Address

GCA/Precision Scientific
3737 W. Cortland St.
Chicago, IL 60647
Attn: Dr. Jim Tison
(312) 227-2660

Dissolved Gases
GAS

Pesticides
PES

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FOR

INSTRUMENTATION FOR MONITORING PESTICIDES

Mnemonic
H2O-PES
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PESTICIDES

A. INTRODUCTION

Pesticides are a category of chemical compounds which are employed to limit, control or eradicate certain life forms adjudged to be undesirable. Pesticides encompass a diversity of chemical types: organic (mostly synthetic), inorganic and organometallic. They cover a wide variety of pest control applications: contact or systemic poisons, repellents or attractants. Popularly, the term "pesticide" may have become almost synonymous with "insecticide"; however, pesticides also include herbicides, fungicides, algicides, rodenticides, nematocides and others.

Much has been written about problems of pesticides in the environment, both in the technical and lay literature. Broad scale public awareness of ecological hazards associated with pesticides generally stems from Rachel Carson's advocative and allegorical 1962 book, Silent Spring (Ref. 1). Despite its controversial nature, Silent Spring is a useful reference to early research on pesticide pollution. Rudd's Pesticides and the Living Landscape (Ref. 2) has been cited as a more balanced early review of this situation (Ref. 3). Other references may be found in a bibliography, Pesticides in Soils and Water (Ref. 4) and in the proceedings of symposia: Research in Pesticides (Ref. 5), Agriculture and the Quality of Our Environment (Ref. 6), Organic Pesticides in the Environment (Ref. 7), Chemical Fallout -- Current Research on Persistent Pesticides (Ref. 8), Fate of Organic Pesticides in the Aquatic Environment (Ref. 9), among others. Government publications bearing on pesticide pollution of the environment include Water Quality Criteria (Ref. 10), Ecological Effects of Pesticides on Non-Target Species (Ref. 11), Effects of Pesticides in Water - A Report to the States (Ref. 12), and Report of the Secretary's Commission on Pesticides and Their Relationship to Human Health (Ref. 13). Relatively recent publications which significantly survey pesticide pollution include Persistent Pesticides in the Environment (Ref. 3) and Pesticides in the Environment (Ref. 14). Publications dealing specifically with the detection, identification and assay of pesticides in the environment are cited separately under section B. Scientific and lay periodicals dealing with pesticide pollution are not limited to those cited herein.

1. Historical Aspects

A brief review of the history and scope of pesticides follows, based in part on References 3, 14-16.

Insect spray, weed killer, rat poison, fungistats, antiseptics and so on have become so commonplace today that it is hard to imagine life without chemical agents to combat pests. Yet few such chemicals existed a century ago. Synthetic organic chemical pesticides were virtually unknown. Natural organic compounds found limited use, many without recognition of their specific chemical identity. Examples include:

pyrethrum (ground chrysanthemum [*C. Cinerariaefolium*] flowers) -- insecticide

nicotine (aqueous tobacco leaf extract) -- fumigant and contact poison against aphids, etc. -- insecticide

herbs and spices to preserve food -- fungistats, bacteristats

herbaceous teas to scourge alimentary parasites -- antihelminthics

soap, vinegar, alcohol, turpentine -- diverse pesticidal applications; antiseptics

garlic necklaces worn as good health charms (now known to repel malaria mosquitos, among others) -- insect repellent.

In the 19th and early 20th century inorganic pesticides found wider usage than presently. In general, their toxicity was broad, i.e., relatively non-specific. Examples include:

"Bordeaux mixture," (cupric sulfate, quick lime and water) to prevent blight, first with grapes, later with potatoes and other vegetables -- fungicide

"Paris Green" (cupric aceto-arsenite), used with success against the Colorado potato beetle, among others -- insecticide

sulfur dust -- fungistat

lead arsenate -- insecticide

"cyanide gas" (hydrogen cyanide, HCN) for extermination of insects and vermin within controlled atmospheres -- biocidal fumigant

sulfuric acid (H_2SO_4), broad leaf weed killer -- herbicide

Some of these early pesticides continue in use today, e.g., pyrethrum or its active principles (pyrethrins, cinerins), cyanide (HCN), cupric (Cu^{++}) salts, and sulfur dusts. However, more frequently the early pesticides, particularly those which were inadequate, costly or broadly toxic, have been replaced over the years. For example, prior to DDT (1939), petroleum distillates were employed widely as insecticide sprays. Material costs were low but so was the effectiveness. Present applications of distillates are confined to domestic uses (homes and gardens) or as spray solvents for organic pesticides (pyrethrins, DDT, dieldrin, etc.). Also prior to DDT, rotenone, the natural organic fish toxin extracted from derris root, achieved some success as a contact poison against insects (e.g., raspberry beetles, human lice, etc.). Rotenone is readily biodegradable, which gives it comparative safety towards mammals and birds.

The use of heavy metals (e.g., arsenic, mercury, lead) as pesticides is declining for reasons of expense, general toxicity (non-specificity) and, in some cases, environmental accumulation (non-degradability). Cupric ion (Cu^{++}) is a partial exception. In water it is relatively harmless to birds and mammals below 1 mg/l, hence copper sulfate is still employed as an algicide in pools, ponds and watercourses. Many fish species suffer toxic effects at these levels, so the application must be chosen with care. Organomercurials constitute the most significant mixed organic-inorganic pesticides. Mercury is a matter of concern throughout the environment (see section on metals, H2O-MET; also Vol. 1, section AIR-HG, and Vol. 4, section BIO-MET), yet organomercurials may be necessary as fungicides (e.g., on seed grain) despite poisoning accidents.

Herbicides have also been characterized by broad, general toxicities. Early use of organic compounds to replace inorganics involved synthetic dinitroaromatics such as dinitro orthocresol. Originally they were employed as insecticides. In 1942 herbicides took a significant step forward with the introduction of synthetic plant hormones to induce defective growth. Derivatives of phenoxyacetic acid ($C_6H_5OCH_2CO_2H$) and 2-phenoxypropionic acid are the most widely used; examples include the familiar 2,4-D and 2,4,5-T. Although these herbicides are not particularly selective among plants, their acute toxicity is largely limited to plants and generally they are readily biodegradable.

No historical sketch on pesticides, however brief, would be complete without noting the immense impact of the synthetic organics since 1939 when the potent toxicity of DDT (2,2 -bis-(p-chlorophenyl-1,1,1-trichloroethane) toward insects in particular was first appreciated. This, coupled with its low cost and comparative safety to mammals (including man) and plants, provided DDT with seemingly miraculous insecticidal properties which revolutionized the concept of insect control.

DDT was instrumental in curtailing the threats of malaria and typhus epidemics toward the end of World War II through abatement of their respective carriers, the *Anopheles* mosquito and the human body louse. Subsequent general agricultural use of DDT gave immediate relief to crops from insect depredations without noticeable initial adverse environmental effects when proper controls were observed. Soon, however, the principle survivors of an insect pest species were those which were comparatively resistant to DDT. The great reproductive capacity of insects permitted the resistant survivors to proliferate unchecked by either DDT or their natural insect predators, also reduced by DDT. Ever increasing doses of DDT were required to control resistant strains. This, along with the persistence of DDT in the environment, eventually led to the present situation in which DDT has accumulated throughout the world as an environmental pollutant. Other chlorinated hydrocarbon insecticides which followed DDT (e.g., dieldrin, aldrin, lindane, heptachlor, chlordane) can pose similar problems.

Insect strains which have become resistant to chlorinated hydrocarbons fail to possess any particular immunity to other types of insecticides; hence, periodic pesticide rotation may offer a partial solution to resistance development. Presently, the large scale alternatives to chlorinated hydrocarbon insecticides are limited to the cholinergic organophosphates (parathion, methyl-parathion, malathion, TEPP, etc.) and carbamates (e.g., carbaryl, isolan, zectran). These types of insecticides have the advantage of being degradable in the environment within days and weeks vs. the years required for DDT and its genre.

Clearly, facile degradability to harmless products is as important with pesticides as relative specificity for the target pest; otherwise, accumulation can pollute the environment. Among pesticides presently in use, the chlorinated hydrocarbon insecticides pose the greatest environmental threat. Heavy metal pesticides, particularly arsenic (As) and mercury (Hg), deserve attention where they are still utilized. Because they are general nerve toxins, organophosphorus and carbamate insecticides must be employed with great care, even though most are fairly rapidly degradable.

2. Characteristics

Pesticides have been classified according to use; however, since this discussion deals with pesticides as aquatic pollutants, classification based on physical and chemical properties is more relevant than the original use. Inorganic pesticides have extremely limited present commercial applications and are more properly discussed as inorganic pollutants under individual sections, e.g., arsenic or mercury under METALS (H2O-MET). Similarly, mixed organic-inorganic (organomercurials, organoarsenicals) compounds are also covered there.

Organic compounds constitute the bulk of chemical pesticides in current use. Distinctions may be drawn between natural and synthetic organics; however, commercial synthesis of natural organic pesticides (botanicals) is by no means precluded. The chemical origin of organic pesticides thus has little bearing on their effect on the environment *except* in one important sense: synthetic pesticides *may* be produced which are much more resistant to environmental degradative processes than natural organic compounds. *In fact, non-degradability is the most important single aspect of environmental contamination by pesticides.* For this reason primary emphasis is given here to those synthetic pesticides which persist in the environment.

In the U.S., most surface waters and their sediments studied contain chlorinated hydrocarbon insecticides, particularly DDT and its degradation products, as well as some herbicides such as 2,4-D. The concentrations in water are generally in micrograms per liter ($\mu g/l$) or less, but concentrations in sediments or particulate matter can be much higher. Arsenic and some herbicides also persist in some soils (Ref. 17).

2.1 Chemical Classification

Names and chemical structures of some important synthetic organic pesticides appear in Table 1.

2.2 Formulation

Synthetic organic pesticides normally are produced as concentrates to be formulated before application, often at rates of well below 1 pound per acre. Formulations (0.1 to 95% pesticide) include dusts, impregnated granules, solutions, emulsions, or suspensions of wettable powders, based on diluents such as clays, talc, water or organic solvents (Ref. 17). Adsorption of pesticides on clay particles improves control during application with less dissipation of the chemical into atmosphere and other nontarget areas (Ref. 10).

2.3 Physical Characteristics

Both among and within chemical classes, the properties of pesticides can differ widely, including their potential for environmental contamination. Particularly important are the tendencies to vaporize, to dissolve in water and other solvents, and to resist various degradative processes. Selected physical constants of 32 organic pesticides (Table 2) were compiled from several sources by Faust and Suffet (Ref. 18).

It would be simple to estimate the maximum concentrations of dissolved pesticides in natural waters using temperature and solubility data (see Table 2), except that natural waters contain organisms, suspended solids, dissolved minerals and organic matter which affect the physical condition of pesticides in water (Ref. 17). For example:

(a) They may be adsorbed on solid particles.
(b) They may be dissolved in fatty substances.
(c) They may form complexes or otherwise associate with organic materials.

2.4 Production and Utilization

In 1964, more than 100 million acres of the continental United States were treated with some kind of pesticide (Ref. 10). Nearly 1 billion pounds of pesticides were applied in 1970, about half on farms and the other half for public/governmental purposes (Ref. 11).

Total production figures (including exports) show more than 1 billion pounds were produced in 1967, 18% higher than in 1965 (Ref. 4) and more than five times 1945 levels (Ref. 10). Table 3 indicates that synthetic organic chemical pesticides are the most important of these compounds, in both quantity produced and potential for contaminating the environment. Annual domestic consumption of *organics* in 1969 was around 800 million pounds (Ref. 17).

2.5 Degradation Products

When considering organic pesticide residues in the aquatic environment, it is important to include biological degradation products (metabolites) and chemical degradation products (e.g., from hydrolysis or oxidation). Examples are shown in Figures 1 and 2. Degradation by chlorine in water and sewage treatment plants is also possible. Some of these derivatives may be more toxic than the parent molecule or cause taste and odor problems. Since knowledge of their concentrations may also give insight concerning the occurrence and/or persistence of organic pesticides, analysis for metabolites, oxidation and hydrolysis products from natural and treated waters is important (Ref. 18).

2.6 Chlorinated Hydrocarbons

For two decades chlorinated hydrocarbons such as DDT, dieldrin, aldrin, lindane (γ-BHC), and heptachlor (see Table 1) enjoyed unprecedented success as insecticides. However, early in the 1960's widespread, long-term environmental effects became apparent. Worldwide environmental accumulation is the natural consequence of (a) large scale applications, (b) environmental half-lives measured in years and decades, and (c) volatilities which permit environmental distribution

Table 1

CHLORINATED HYDROCARBON INSECTICIDES

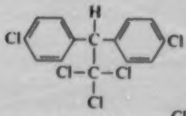
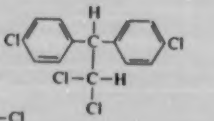
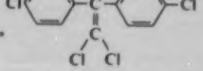
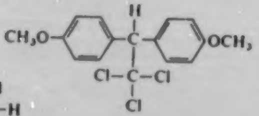
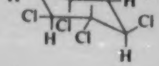
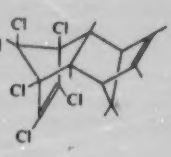
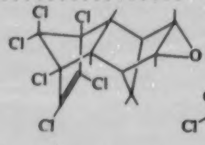
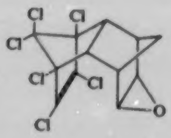
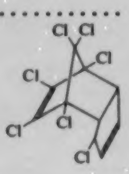
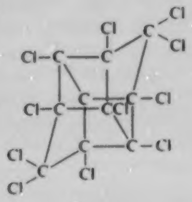
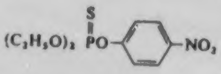
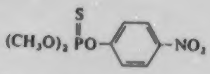
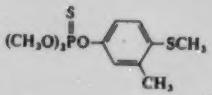
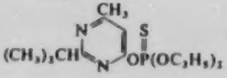
Common Name	Chemical Name	Structural Formula
DDT	2,2-bis(*p*-chlorophenyl)-1,1,1-trichloroethane	
DDD, TDE	2,2-bis(*p*-chlorophenyl)-1,1-dichloroethane	
DDE	2,2-bis-(*p*-chlorophenyl)-1,1-dichloroethylene	
Methoxychlor	2,2-bis(*p*-methoxyphenyl)-1,1,1-trichloroethane	
γ-BHC, Lindane	γ-1,2,3,4,5,6-hexachloro-cyclohexane	
Aldrin	1,2,3,4,10,10-hexachloro-1,4-4a,5,8,8a-hexahydro-1,4-*endo-exo*-5,8-dimethanonaphthalene	
Dieldrin	1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo-exo*-5,8-dimethanonaphthalene	
Endrin	1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo-endo*-5,8-dimethanonaphthalene	
Heptachlor	1,4,5,6,7,8,8-heptachloro-3a-4,7,7a-tetrahydro-4,7-*endo*methanoindene	
Mirex	dodecachlorooctahydro-1,3,4-metheno-2H-cyclobuta[cd] pentalene	
ORGANOPHOSPHORUS INSECTICIDES		
Parathion	*O,O*-diethyl-*O*-*p*-nitrophenyl phosphorothioate	
Methyl Parathion	*O,O*-dimethyl-*O*-*p*-nitrophenyl phosphorothioate	
Fenthion, Baytex	*O,O*-dimethyl *O*-3-methyl-4-methylthiophenyl phosphorothioate	
Diazinon	*O,O*-diethyl *O*-2-isopropyl-4-methylpyrimidyl-6 phosphorothioate	

Table 1 (continued)

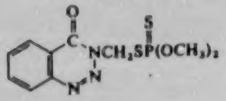
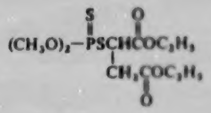
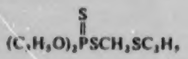
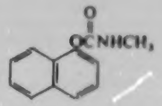
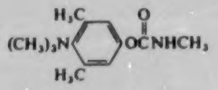
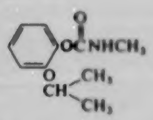
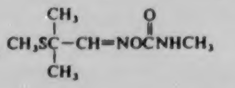
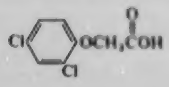
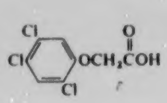
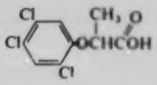
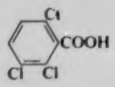
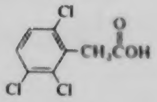
Common Name	Chemical Name	Structural Formula
Axinphosmethyl, Guthion	*O,O*-dimethyl *S*-4-oxo-1,2,3,-benxotriazine-(4*H*)-yl-methyl phosphorodithioate	
Malathion	*O,O*-dimethyl S-(1,2,-dicarbethoxyethyl) phosphorodithioate	 $(CH_3O)_2-\overset{S}{\overset{\|}{P}}SCH\overset{O}{\overset{\|}{C}}OC_2H_5$, $CH_2\underset{\underset{O}{\|}}{C}OC_2H_5$
Phorate, Thimet	*O,O*-diethyl-*S*-(ethylthio) methyl phosphorodithioate	 $(C_2H_5O)_2\overset{S}{\overset{\|}{P}}SCH_2SC_2H_5$
CARBAMATE INSECTICIDES		
Carbaryl, Sevin	N-methyl-1-naphthylcarbamate	
Zectran	4-dimethylamino-3,5-xylenyl N-methylcarbamate	
Baygon	2-isopropoxyphenyl N-methylcarbamate	
Temik	2-methyl-2-(methylthio)-propionaldehyde O-(methylcarbamoyl)oxime	 $CH_3S\overset{CH_3}{\underset{CH_3}{C}}-CH=NO\overset{O}{\overset{\|}{C}}NHCH_3$
HERBICIDES		
2,4-D	2,4-dichlorophenoxyacetic acid	
2,4,5-T	2,4,5-trichlorophenoxyacetic acid	
Silvex, Fenoprop	2-(2,4,5-trichlorophenoxy) propionic acid	
2,3,6-TBA	2,3,6-trichlorobenzoic acid	
Fenac	2,3,6-trichlorophenylacetate	

TABLE 2.

Physical Constants of Selected Organic Pesticides (from Ref. 18).

Compound	Molecular Weight	Physical State	Melting or Boiling point, °C	Vapor Pressure, torr (°C)	H_2O Solubility, µg/1	(°C)
Aldrin	364.93	Solid	104-104.5	6×10^{-6} (25)	0.20	(25)
Altrazine	215.7	Solid	173-175	—	70	(27)
γ-BHC	290.83	Solid	112.9	9.4×10^{-6} (20)	10	(20)
CIPC	213.7	Solid	36-40	—	108	(20)
cis-Chlordane	409.8	Liquid	175 at 2 mm	—	—	
2,4-D	221	Solid	140.5	0.4 (160)	620	(25)
DDD (TDE)	320.05	Solid	109	—	—	
DDT	354.49	Solid	108.5-109	1.5×10^{-7} (20)	0.0017	(25)
DDVP	221.0	Liquid	84 at 1 mm	0.032 (31)	10000	(24.5)
Demeton	258.0	Liquid	134 at 2 mm	10^{-3} (33)	100	
Diazinon	204.3	Liquid	83-84 at 0.002 mm	1.4×10^{-4} (20)	40	(room)
Dieldrin	380.91	Solid	175-176	1.8×10^{-7} (25)	0.14	
Dimethoate	229.3	Solid	51-52	0.025 (25)	7000	
Diuron	233.1	Solid	150-155	3.1×10^{-6} (50)	42	(25)
Endrin	380.91	Solid	> 200	2×10^{-7} (25)	0.19	
Fenthion	278.3	Liquid	105 at 10^{-2} mm	—	5.3-6.0	(20)
Fenuron	164.2	Solid	127-129	1.6×10^{-4} (60)	2900	(24)
Heptachlor	373.34	Solid	95-96	3×10^{-4} (25	—	
IPC	179.2	Solid	66.5-68.5	—	20-25	
Malathion	330.36	Liquid	156-157 at 0.7 mm	4.0×10^{-4} (30)	145	
Methoxychlor	345.65	Solid	89	—	0.10	(25)
Parathion	291.26	Liquid	157-162 at 0.6 mm	0.03 (24)	24	(25)
Phorate	260.4	Liquid	118-120 at 0.8 mm	3.9×10^{-3} (36)	85	
Phosdrin	224.0	Liquid	99-103.3 at 0.03 mm	2.9×10^{-3} (21.1)	—	
Ronnel	321.4	Solid	35-37	8×10^{-3} (25)	800	
Simazine	201.7	Solid	225-227	6.1×10^{-9} (20)	5.0	(20)
2,4,5-T	255.5	Solid	158	—	251	(25)
2(2,4,5-TP)	269.5	Solid	179-181	—	140	(25)
PCP	266.4	Solid	190-191	0.12 (100)	14	(20)
DNBP	240.2	Solid	39.4	—	1000	(25)
DNC	198.1	Solid	85.8	1.05×10^{-6} (25)	125	
Sevin	201.2	Solid	145	—	< 1000	

TABLE 3.

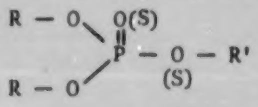
Approximate Production of Pesticidal Chemicals, United States: 1965-1967
(from Ref. 17).

Chemical	1965 1000 pounds	1967 1000 pounds
Fungicides:		
Copper naphthenate	3,268	3,473
Copper sulfate	47,272	33,992
Ferbam	2,384	2,331
Mercury fungicides	1,602	912
Nabam	2,489	1,361
Pentachlorophenol (PCP)	39,965	44,239
2,4,5-Trichlorophenol and salts	4,003	14,008
Zineb	5,075	3,055
Other organic fungicides	44,969	63,269
Total	151,027	166,640
Herbicides:		
2,4-D acid, esters and salts	63,360	83,750
DNBP	4,619	N.A.
DNBP, ammonium salt	59	58
Phenyl mercuric acetate (PMA)	588	518
Sodium chlorate	32,000	30,000
2,4,5-T acid, esters and salts	13,516	27,189
Other organic herbicides	105,861	206,759
Total	220,003	348,274
Insecticides, fumigants, rodenticides:		
Aldrin-toxaphene group	118,832	120,183
Calcium arsenate	4,192	2,500
DDT	140,785	103,411
Dibromochloropropane	3,433	5,240
Lead arsenate	7,098	6,000
Methyl bromide	14,303	19,665
Methyl parathion	29,111	33,344
Parathion	16,607	11,361
Other organics	167,368	202,600
Total	501,729	504,304
Grand Total	872,759	1,019,218

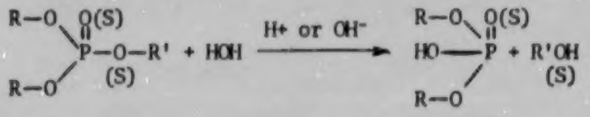
in conjunction with the water cycle (co-distillation and co-condensation). Recently concern has arisen in connection with other chlorinated hydrocarbons which also accumulate in the environment, particularly the polychlorinated biphenyls (PCBs). Until recently large quantities of PCBs were synthesized for a variety of industrial uses (Ref. 19).

2.7 Organophosphates

As seen in Table 1, most organic phosphorus insecticides have the general phosphate structure:



where R is an alkyl group and R' is an organic radical. Four types of general structure are possible when either oxygen or sulfur is substituted as indicated (Ref. 18): Organophosphate pesticides tend to hydrolyze to relatively harmless products as follows:



Activation reactions, i.e., the conversion of a poorer to a stronger cholinesterase inhibitor, occur in the organophosphate pesticides, the major one being $> P = S$ to $> P = O$. This reaction to form the more toxic "oxon" may occur by chemical

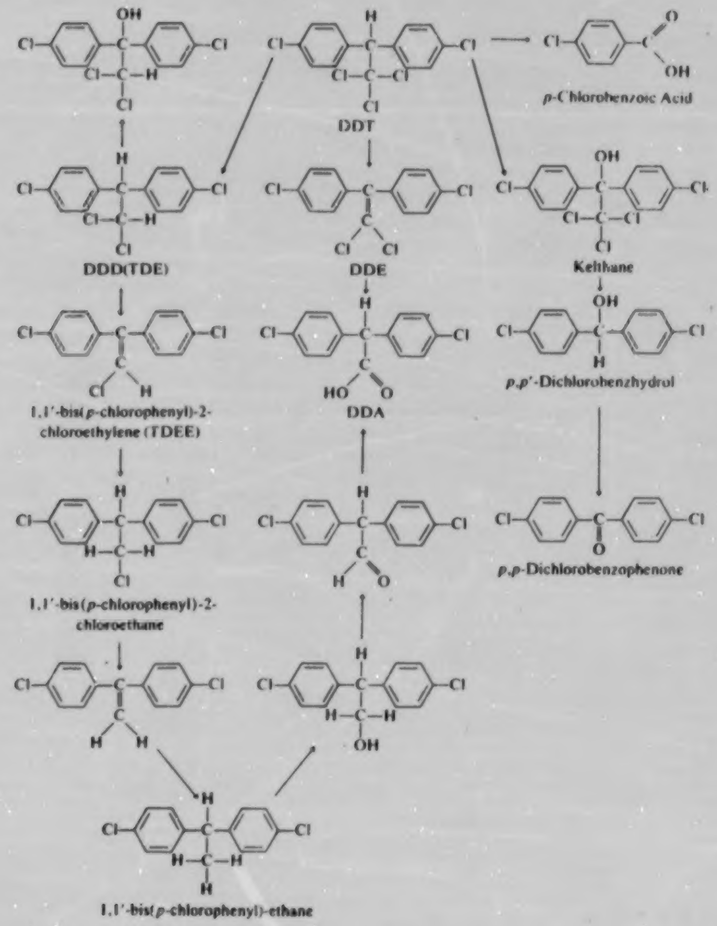

DDT
p-Chlorobenzoic Acid
DDD(TDE)
DDE
Kelthane
1,1'-bis(p-chlorophenyl)-2-chloroethylene (TDEE)
DDA
p,p'-Dichlorobenzhydrol
1,1'-bis(p-chlorophenyl)-2-chloroethane
p,p-Dichlorobenzophenone
1,1'-bis(p-chlorophenyl)-ethane

Figure 1: Metabolites of DDT (from Ref. 18)

or enzymic mechanisms (Ref. 20). Organophosphates may also yield other metabolites. For example, sulfoxides and sulfones of fenthion (Baytex) are generated in bean plants (Ref. 20). Metabolic pathways for parathion, malathion, demeton, and phorate have also been elucidated.

2.8 Phenoxyalkanoic Acids

Names and chemical structures of three common phenoxyacid herbicides are given in Table I. The metabolic fate of 2,4-D and its organic esters in bean plants, cows, peas, tomato plants, soil and aquatic microorganisms, etc., has been studied extensively (Ref. 5). Several metabolites have been isolated and identified (see Fig. 2). One of these, 2,4-dichlorophenol, imparts an undesirable taste and odor to drinking water (Ref. 21).

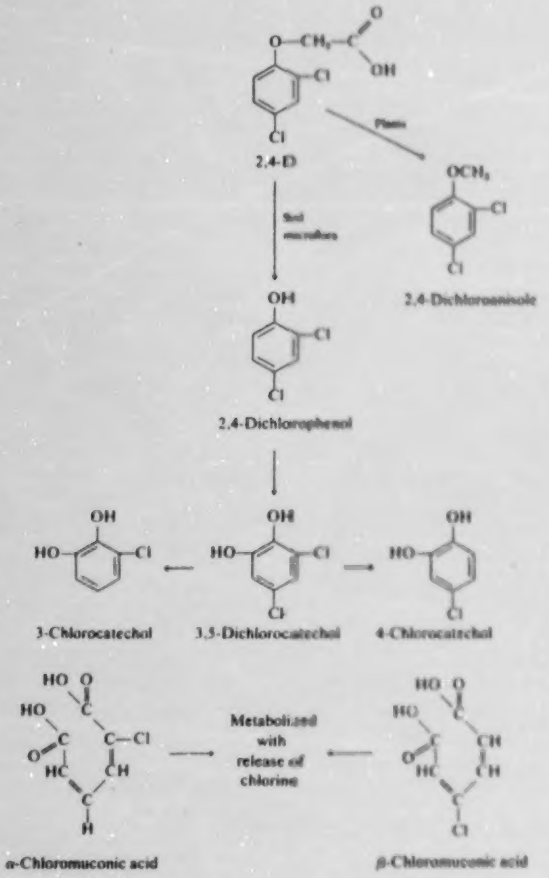


Figure 2: Metabolites of 2,4-D (from Ref. 18).

3. Pesticides and the Aquatic Environment

Since 1945, organic pesticides have been reported in drinking, recreational, irrigational, and fishing waters, as well as in sediments and bottom muds. Early evidence was derived from observations of physiological responses of aquatic organisms; however, since the early 1960's instrumental analysis has been used to detect, identify and quantitate pesticide extracts from natural waters and associated solids (Ref. 18). Examples are shown in section B.

3.1 Sources

Organic pesticides may enter the aquatic environment in the following ways (Ref. 3, 18):

a) direct application for control of aquatic weeds, trash fish, and aquatic insects;

b) percolation and runoff from agricultural lands (primarily in sediment);

c) airborne drift from aerial and land applications (dust, spray);

d) discharge of industrial waste waters (e.g., from pesticide producers);

e) discharge of waste waters from cleanup of equipment used for pesticide formulations and application;

f) atmospheric co-precipitation of vapors and particles with rain.

3.2 Pesticides in Surface Runoff

First results published from the pesticide monitoring program (Ref. 22) indicate chlorinated hydrocarbons in 38 samples of water from 10 rivers: Prior to 1963 DDT was found in the Susquehanna, Delaware, Chattahoochee, Tennessee, Rio Grande, San Joaquin, Sacramento, Yakima, and Columbia Rivers; dieldrin was identified in the Savannah River. Methods of analysis included activated carbon adsorption, infrared spectrophotometry and flame-ionization gas chromatography (GC). Sensitivity was about 1 μg/l. A second study (Ref. 23) identified dieldrin, endrin, DDT and DDE, in that order of frequency, in all major U.S. river basins in concentrations ranging from 4 to 118 ng/l. Evidence for other pesticides was discussed. Updated analytical methods were used: liquid-liquid extraction, thin-layer chromatography (TLC) and microcoulometric GC (Ref. 17). A third study in this series (Ref. 24) involved analyses using TLC, electron-capture GC and microcoulometric GC techniques on 600 samples collected annually from over 100 stations from 1958 through 1965. Highlights of the results were:

a) Dieldrin was the principal residue in all river basins at levels of 1 to 22 ng/l.

b) In 1963, endrin residues reached 214 ng/l in the lower Mississippi, thereafter decreasing to 116 ng/l in 1965.

c) DDT and related compounds have been common in surface waters since 1958.

d) Aldrin, BHC, heptachlor, and heptachlor epoxide were also detected (ng/l).

Appendix 1 (q.v.) contains the fourth and most comprehensive national pesticide survey, published in 1970 by Lichtenberg *et al.* (Ref. 25). Five annual surveys (1964 through 1968) were conducted which demonstrated the first observable decline in aquatic chlorinated hydrocarbon residues (Fig. 3 in App. 1). Even so, chlorinated hydrocarbons can remain stable in soil and eventually permeate into surface and ground water. Thus, detectable traces may continue into the future despite sharply restricted usage.

DDT residues transported by the Mississippi River into the Gulf of Mexico have been estimated at 10 metric tons annually, or about half the estimated total river output from the continental U.S. U.S. application of DDT between 1961 and 1968 ranged from 54 to 80 thousand metric tons/year, several thousand times more than the above estimate. It would seem, then, that only a fraction of the annual production of DDT reaches the oceans by runoff (Ref. 19).

3.3 Pesticides from Atmospheric Transport

DDT residues enter the atmosphere by several routes, e.g., aerosol convection during application, and vaporization from water surfaces (Ref. 26), plants and soils (Ref. 27). Once in the atmosphere DDT may travel great distances, returning to land or sea in precipitation or in dry fallout. DDT residues in precipitation were found in Great Britain at seven stations in 1966 to 1967. The mean concentration was 80 ng/l (Ref. 28), about twice that reported for meltwaters of recent antarctic snow (Ref. 29). DDT residues in South Florida precipitation averaged 1 ng/l in 18 samples taken at four sites in 1968 to 1969 (Ref. 30).

If the total annual precipitation of water over the oceans, estimated as 3×10^{17} liters (Ref. 19), averaged 80 ng/l DDT (as above), 24,000 metric tons of DDT residues would be precipitated each year into the oceans. *Thus the atmosphere may be a major route for transfer of DDT residues into the oceans* (Ref. 19). Other chlorinated hydrocarbons with similar physical and chemical properties **should behave analogously, e.g.,** dieldrin readily volatizes into the atmosphere (Ref. 31) and has been found in rainwater along with PCBs (Ref. 28). Presumably the atmospheric transport cycle also operates over land, but perhaps less extensively because of sorption processes by soil and organic matter.

3.4 Pesticides in Fauna

Pesticide residues in tissue of land-based mammals, reptiles and birds originate normally via contaminated food (Ref. 3). Primarily these are the chlorinated hydrocarbons (most others are metabolized). This is also true for the aquatic environment but with two important additional routes. The tendency of some pesticides to be adsorbed on particles suspended in the water allows pesticides to be concentrated by filter-feeding organisms (Ref. 3, 17). Also, there is evidence that aquatic organisms acquire residues directly through the gills and skin (Ref. 32). Pimentel (Ref. 10, Part V) has provided an excellent referenced summary on pesticide residues in fauna.

The relation of pesticides to fauna is illustrated by studies of two areas -- California and Antarctica. Between 1963 and 1965, 2100 samples were collected from 86 species of California wildlife and their environments and analyzed (Ref. 33). Residues of chlorinated hydrocarbon pesticides were found throughout California, both in wildlife and in their environment. Species from aquatic or wetland habitats carried heavier insecticide loads than species from dry habitats (up to 70 mg/kg for shore birds). Exceptions among the dry-land species were carnivorous forms, e.g., raptorial birds (up to 60 mg/kg). Most water samples contained residues. Particulate matter suspended in water generally contained 10,000 to 100,000 times the residue remaining in the water after filtration.

Animals from areas not treated with DDT usually contained residues in their fatty tissue: Tule elk averaged about 14 mg/kg DDT and metabolites in their fat, comparable to man. Water fowl and raptorial birds showed moderate to high values of DDT, toxaphene, and dieldrin. Fish, including anadromous species, contained residues with the highest loads in top-level predators.

Pesticide residues in Antarctic wildlife (Ref. 34, 35) were very low, generally below 1 mg/kg. Only certain groups of animals contained measurable residues. Residues were not initially found in the physical environment, but later appeared in snow and water (Ref. 29). The highest residues found were:

DDE - skuas (type of seabird), 2.8 mg/kg
DDT - fish, 0.44 mg/kg
DDT - penguins, 0.18 mg/kg
DDT - seals, 0.12 mg/kg

Only skuas range beyond the Antarctic shelf.

Edwards (Ref. 3) has summarized and collated extensive data on pesticide residues in fauna. Virtually all fauna, especially those associated with the aquatic environment, show pesticide residues with those living atop food chains showing the greatest accumulation.

4. Effects of Pesticide Pollution

Aquatic pesticide residues may reach humans through drinking water, but the concentrations in most cases are far below toxic levels. The chief known hazard of aquatic residues is the concentration of chlorinated hydrocarbons in the food chain (biological magnification): e.g., absorption of pesticides by plankton, which are food for aquatic insects, small fish, etc., which in turn are eaten by larger fish and ultimately by man. Failure to metabolize these residues permits their progressive buildup at each stage. Biological magnification occasionally occurs in our own food chain (e.g, game fish and fowl; chicken raised on tuna meal). Biological magnification is more serious with fish and wildlife, particularly with the reproduction of top-level predators. Pimentel (Ref. 11) has collated extensive toxicological data on insecticides, herbicides, and fungicides.

4.1 Effects on Man

4.1.1 Acute Exposure

Human fatalities have resulted from most of the major pesticides, and virtually all pesticides can cause illness (Ref. 17). It is difficult to evaluate the hazard to man on the basis of animal data (Ref. 36) because the toxicity of a pesticide varies from species to species. A manual on the safe use of pesticides is available (Ref. 37).

Illness due to food contaminated by pesticides has been more common abroad (Ref. 17); however, in this country, people eating crops within a few days of toxaphene nicotine application have become seriously ill. The residues amounted to fractions of a percent, far above the established tolerances.

4.1.2 Chronic, Low-Level Exposure

Results of studies generally agree that humans now carry 10 to 20 mg/kg of chlorinated hydrocarbon insecticides and their conversion products in fatty tissue (Ref. 17, 38). Most of this is DDT and related materials, but the total also includes dieldrin, BHC, and heptachlor epoxide. DDT has been measured for a significant length of time and appears to have reached a steady state in human body fat in the U.S. Levels for other chlorinated hydrocarbons not in use as long are much lower.

Volunteers have ingested 35 milligrams of DDT per day for periods of 21 months with no detectable effect except that they stored and excreted more DDT breakdown products than they would have normally. The dosage was about 1000 times that found in restaurant meals in the U.S. in 1962 (Ref. 38). Mortality and morbidity data in the U.S. reveal no serious trends correlating with the rise of DDT (Ref. 17).

4.2 Agricultural Effects*

Pesticide residues have concerned livestock owners since their first use. Since the cheapest diluent is water, even for relatively insoluble coupounds, leftover formulations may be unintentionally consumed by thirsty livestock, or may enter the water supply through improper disposal. Pesticides found in food may be considered adulterants or additives resulting in condemnation of meat, milk, or other products.

Biological effects of accumulated pesticides in animal tissue are complicated by the similarity of pathological changes induced by naturally occurring dysfunctions, not all of which are clearly understood. Effects of stress and some dysfunctions related to steroid hormones may result in diseases to poultry also linked to organic phosphates. Arsenic affects phosphorus metabolism; copper affects phosphorus-molybdenum balance.

4.3 Estuarine Effects

In spite of improved control of pesticide usage, drainage from land runoff into estuaties and coastal areas renders important fishing industries vulnerable to toxic effects (Ref. 10). Examples include estuarine oyster populations, juvenile shrimp, crab, and menhaden which occupy the habitat where fresh and salt water mix and where deposition of river silt with its load of adsorbed pollutants takes place. These economically important animals are especially sensitive to low levels of pesticides. Approximately 1 μg/kg DDT or PCB is lethal to shrimp and crab (Ref. 19). At 0.1 μg/kg DDT in estuarine water, oyster production is only 20% normal, shrimp populations suffer a 20% mortality, and menhaden suffer a disastrous mortality (Ref. 10). TL_m+ (48 hr) data for exposure of shrimp to 19 insecticides are given in Table V.

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*Condensed from the National Technical Advisory Committee Report (Ref. 10)

+Tolerance Limit, median (see glossary).

Table 4
48 hr TL_m *of Insecticides on Shrimp, µg/l (from Ref. 10).*

	Organochloride pesticides		
Aldrin	0.04	DDT	0.6
BHC	2.0	Dieldrin	0.3
Chlordane	2.0	Endosulfan	0.2
Endrin	0.2	Methoxychlor	4.0
Heptachlor	0.2	Perthane	3.0
Lindane	0.2	TDE	3.0
		Toxaphene	3.0
	Organophosphorus pesticides		
Coumaphos	2.0	Naled	3.0
Dursban	3.0	Parathion	1.0
Fenthion	0.03	Ronnel	5.0

Information condensed from the National Technical Advisory Committee Report (Ref. 10) follows:

Although chlorinated hydrocarbons may be degraded in living systems into less toxic metabolites, when they are trapped in soil and estuarine sediments they may persist unchanged for years and continue to threaten animal communities. Organophosphorous insecticides typically break down into less toxic products much more readily than chlorinated hydrocarbons; some last only a few days in the environment. They exhibit a wide range of toxicity, both more and less damaging to marine fauna than chlorinated hydrocarbons. Other major chemical categories, (e.g., carbamates, arsenicals, 2,4-D and 2,4,5-T) are generally less toxic to estuarine and marine biota.

The extreme sensitivity of estuarine and marine crustaceans, such as crabs, lobsters, and shrimp, to the array of insecticides is expected because of their close phylogenetic relationship with terrestrial arthropods. Generally shrimp are also much more sensitive than fish or oysters to other pesticides. This plus their economic importance make shrimp a critical species for establishing safe levels of pesticides in estuarine environments (see Table 4; also section 5.3).

4.4 Wildlife Effects

Pesticide levels in the aquatic environment affect the health, reproduction, and natural growth of wildlife. DDT residues in wildlife are widespread (see section 3.4 above). Keith and coworkers (Ref. 40, 41) reported 14 µg/kg of DDT and its metabolites in lake bottom muds. About 50 times that level occurred in amphipods, 500 times as much in fish and old squaw ducks, and 15,000 times as much in herring gulls that ate the fish; reproduction of the gulls decreased.

Wurster (Ref. 42) has summarized problems of chlorinated hydrocarbons in food chains:

> "The compounds increase in concentration with increasing trophic level, generally reaching highest concentrations in carnivores, including carnivorous birds. On at least two continents, a pattern of diminished reproductive success of carnivorous birds coincides with the presence of chlorinated hydrocarbon residues, particularly those of DDT. Included are such birds as grebes, woodcock, various birds of prey, seabirds, and possibly others that have not been studied, although exceptions to these correlations exist. Additional information comes from various laboratory experiments and field observations including feeding experiments, egg injections, bird behavior, chick mortality, eggshell weight measurements, and enzyme induction. The data suggest that these chemicals interfere with calcium metabolism and hormonal mechanisms. Two mechanisms involving calcium metabolism are proposed to explain these observations:
>
> 1. Acute toxicity involves direct attack on the nerve axon with associated axon decalcification and symptons of calcium deficiency. This mechanism can kill adult birds or chicks shortly after hatching.
>
> 2. Chlorinated hydrocarbons cause induction of hepatic enzymes that metabolize steroid hormones; estrogen breakdown is especially important, since estrogen influences calcium metabolism in birds. This would explain the widespread occurrence of calcium-deficient eggshells among carnivorous birds since introduction of DDT in the late 1940's. Current knowledge indicates, despite several anomalies, that certain chlorinated hydrocarbon insecticides are a probable cause of the widespread diminished reproduction of carnivorous birds."

Eggshell thinning has occurred in a wide range of species of fish-eating birds and birds of prey since the large-scale use of DDT, as shown by studies of museum eggs, usually coinciding with population decline (Ref. 43, 44). Examples of reproductive failure correlating with chlorinated hydrocarbon residues are evident in mallard ducks (Ref. 45), black ducks

(Ref. 46), bald eagles (Ref. 19, 47), brown pelicans, and peregrine falcons (Ref. 19). Biochemical bases for reproductive incapacitation due to chlorinated hydrocarbon residues are also reviewed in Reference 16.

Chlorinated hydrocarbons have differing effects according to species of birds. In Great Britain, herons carry heavy residue loads without seeming to suffer, whereas other carnivorous birds bearing similar loads are declining (Ref. 17, 48). Other studies have shown ring-necked pheasants in California with almost twice the load of the Western grebe (Ref. 33, 49). Although these high residues seem to inhibit reproduction, the effect is slight with pheasants but devastating with grebes (Ref. 17).

5. Water Quality Criteria

In 1968 the National Technical Advisory Committee on Water Quality Criteria published maximum permissible levels for pesticides in the aquatic environment (Ref. 10). Different sets of criteria were recommended by Subcommittees for:

a) Public Water Supplies
b) Agricultural Uses
c) Fish, Other Aquatic Life, and Wildlife.

It should be noted that water quality *criteria* are intended to be scientific requirements on which a decision is to be made regarding what quality of water is suitable for a particular use. This is distinct from water quality *standards* which can only be established by governmental authority and consist of officially accepted *criteria plus* effective *implementation plans* for pollution abatement measures necessary to meet the accepted criteria (Ref. 50).

5.1 Drinking Water Criteria

The Subcommittee on Public Water Supplies (Ref. 10) adopted drinking water criteria (Table 5) for three pesticide groups: chlorinated hydrocarbon insecticides (DDT, dieldrin, etc.), organophosphate/carbamate cholinergic insecticides (parathion, carbaryl, etc.), and phenoxyalkanoic acid herbicides (2,4-D, 2,4,5-T, etc.).

These criteria were based upon recommendations of the Public Health Service Advisory Committee on Use of the PHS Drinking Water Standards, who in turn were advised by an expert group of toxicologists. They characterized as permissible pesticide residues in drinking water: "those levels which, if ingested over extensive periods, could not cause harmful or adverse physiological changes in man."

Hazards from chlorinated hydrocarbon pesticides in water occur both directly through persistence in their original form over long periods, and indirectly through biological magnification in man's food chain. The values selected by the Public Health Service were set with substantial safety factors for humans. Lower than physiologically safe levels were recommended for aldrin, heptachlor, chlordane, and parathion, because of their objectionable taste and odor.

The limit for cholinergic pesticides was established relative to parathion as 0.1 mg/l parathion equivalent. This is necessary because nearly all organophosphorus pesticides and chloinergic carbamates have "high acute toxicity to mammals and some have even higher toxicity to fish". Ingestion of small quantities over long time periods damages central nervous systems.

5.2 Agricultural Water Criteria

The Subcommittee for Agricultural Uses also recommended that pesticides not exceed levels for the chlorinated hydrocarbons in Table 6 for general farmstead uses (Ref. 10). The Subcommittee endorsed the concept of fish in live-

Table 5
Permissible Concentrations for Organic Pesticides in Public Water Supplies (from Ref. 10)

Pesticide	Permissible Concentrations, μg/l
Aldrin	17.0
Chlordane	3.0
DDT	42.0
Dieldrin	17.0
Endrin	1.0
Heptachlor	18.0
Heptachlor epoxide	18.0
Lindane	56.0
Methoxychlor	35.0
Organic phosphates and carbamates	100.0*
Toxaphene	5.0
2,4-D; 2,4,5-T; and 2,4,5-TP	100.0

**As parathion equivalents in cholinesterase inhibition.*

stock source water as a safety indicator, citing evidence of lower tolerance levels for pesticide residues with fish than with livestock. Accordingly, presence of living fish in agricultural water supplies should indicate their safety for livestock (Ref. 16, p. 344). See Table 6 for examples.

With regard to crops, Table 7 lists herbicide levels in irrigation waters which have damaged crops.

5.3 Estuarine Criteria

The Subcommittee on Fish, other Aquatic Life and Wildlife (Ref. 10) separated estuarine and marine organisms from freshwater life, choosing shrimp as a sensitive indicator life form. They recommended a maximum permissible concentration of 50 ng/l for 13 chlorinated hydrocarbon and 6 organophosphorus pesticides acutely toxic to shrimp at 5 μg/l or less (TL_m data in Table 5).

Group B contained pesticides not acutely toxic to shrimp below 1 mg/l:

- Arsenicals
- Botanicals
- Carbamates
- 2,4-D compounds
- 2,4,5-T compounds
- Phthalic acid compounds
- Triazine compounds
- Substituted urea compounds

For these compounds a maximum permissible concentration of 10 μg/l was recommended. Acute toxicity data were available for approximately 100 other pesticides but it was believed that these chemicals were unlikely to reach the estuarine environment at toxic levels. Criteria established for these chemicals in fresh water should be adequate protection for estuaries.

5.4 Freshwater Criteria

For freshwater the above Subcommittee (Ref. 10) recommended that chlorinated hydrocarbons simply not be permitted, noting that "addition

Table 6
Examples of Fish as Indicators of Water Safety for Livestock (from Ref. 16)

Material	Toxic-Levels mg/l for Fish	Toxic Effects on Animals
Aldrin	0.02	3 mg/kg food (poultry).
Chlordane	1.0 (sunfish)	91 mg/kg body weight in food (cattle).
Dieldrin	0.025 (trout)	25 mg/kg food (rats).
Dipterex	50.0	10.0 mg/kg body weight in food (calves).
Endrin	0.003 (bass)	3.5 mg/kg body weight in food (chicks).
Ferban, fermate	1.0 to 4.0	
Methoxychlor	0.2 (bass)	14 mg/kg alfalfa hay, not toxic (cattle).
Parathion	2.0 (goldfish)	75 mg/kg body weight in food (cattle).
Pentachlorophenol	0.35 (bluegill)	60 mg/l drinking water not toxic (cattle).
Pyrethrum (allethrin)	2.0 to 10.0	1,400 to 2,800 mg/kg body weight in food (rats).
Silvex	5.0	500 to 2,000 mg/kg body weight in food (chicks).
Toxaphene	0.1 (bass)	35 to 110 mg/kg body weight in food (cattle).

TABLE 7

Levels of Herbicides in Irrigation Water at Which Crop Injury Has Been Observed. Data Are for Furrow Irrigation Unless Otherwise Specified (from Ref. 10).

Herbicide	Crop Injury Threshold in Irrigation Water mg/l
Acrolein	Flood or furrow: beans-60, corn-60, cotton-80, soybeans-20, sugar beets-60. Sprinkler: corn-60, soybeans-15, sugar beets-15.
Aromatic solvents (xylene)	Alfalfa->1,600, beans-1,200, carrots-1,600, corn-3,000, cotton-1,600, grain sorghum->800, oats-2,400, potatoes-1,300, wheat-1,200.
Copper sulfate	Apparently, above concentrations used for weed control.
Amitrole-T	Beets (rutabaga)->3.5, corn->3.5.
Dalapon	Beets->7.0, corn-<0.35.
Diquat	Beans-5.0, corn-125.0.
Endothal Na and K salts	Corn-25, field beans-<1.0, alfalfa->10.0.
Dimethylamines	Corn->25, soybeans->25, sugar beets-25.
2,4-D	Field beans->3.5<10, grapes-0.7-1.5, sugar beets-3.5.
Dichlobenil	Alfalfa-10, corn->10, soybeans-1.0, sugar beets-1.0-10.
Fenac	Alfalfa-1.0, corn-10, soybeans-0.1, sugar beets-0.1-10.
Picloram	Corn->10, field beans-0.1, sugar beets-<1.0.

of any persistent chlorinated hydrocarbon pesticides is likely to result in damage to aquatic life...as concentrations of these chemicals increase in the aquatic environment, progressive damage will result...the chronic consequences may not be observed for some time". Although other kinds of chemical pesticides in or around fresh waters may produce a variety of acute and chronic effects on fish and other biota, the Subcommittee felt that due to their lack of persistence, "some of them can be used around water, but only in amounts below those that produce chronic damage to desirable species" In general, the Subcommittee held that "reasonably safe concentrations" in receiving waters of the pesticides in Table 8 could be assured by permitting their levels to rise no higher than 1 to 10% of the 48 hr TL_m values listed in Table 8.

6. Legal Aspects

The marketing and use of pesticides are subject to numerous state laws and regulations and to two basic, interrelated federal statutes:

I. the Federal Insecticide, Fungicide, and Rodenticide Act (Ref. 51)

II. the Federal Food, Drug, and Cosmetic Act (Ref. 52).

The Federal Insecticide, Fungicide, and Rodenticide Act was administered by the Department of Agriculture until authority was transferred to the Environmental Protection Agency (EPA) in December 1970. It requires that all pesticide products shipped in interstate commerce be registered with EPA. Before registration is granted, the manufacturer must provide scientific evidence that the product (a) would be effective against the pest or pests listed on the label, (b) would not injure humans, crops, livestock, wildlife and/or damage the total environment when used as directed, and (c) the directed use would not result in illegal residues on food or feed.

In particular, data on toxicity and safety must be submitted as well as rate of disappearance in the field. Also, adequate means of detecting the pesticide must be furnished, i.e., an analytical method sensitive enough to detect residues at the levels occurring on commodities as they are marketed. *The method must be specific for the pesticide in question and sufficiently simple and practical for use by field laboratories.*

The Federal Environmental Pesticide Control Act of 1972 substantially amends the Federal Insecticide, Fungicide, and Rodenticide Act (Ref. 51) by extending Federal controls to the actual application of pesticides by the user and by regulating intrastate as well as interstate marketing of pesticide products. Intrastate marketing involves about 30,000 pesticide products that will have to be Federally registered after October 1974. Under this statute, penalties may be levied against a purchaser who misuses pesticides.

In particular the 1972 statute:

(a) requires pesticides to be classified for general use or restricted to use by trained applicators;

(b) prohibits the use of any pesticide in a manner inconsistent with labeling instruction;

(c) requires EPA registration of pesticides used in *intra*state commerce;

(d) authorizes EPA to establish pesticide packaging standards, set procedures and regulations for storage and disposal of pesticides and containers, issue experimental use permits, conduct research and monitor pesticide use and presence in the environment;

(e) strengthens enforcement by requiring registration of producers, providing penalties for noncompliance, permitting necessary stop-sale orders and siezure of hazardous pesticides and establishing Federal-State enforcement programs.

All provisions become effective within four years (1976).

The Pesticide Amendment to the Federal Food, Drug, and Cosmetic Act requires that, where necessary to protect the public health, a tolerance or legal limit be established for any residues that might remain in or on a harvested food or feed crop as a result of the application of a chemical for pest control. Tolerances are based on available chemistry and toxicity data showing that the remaining residues are safe. *Establishment* of such tolerance levels is now the responsibility of EPA while *enforcement* of tolerances is the responsibility of the FDA. Pesticides also fall under the Food Additive Regulations to the Food, Drug, and Cosmetic Act. [Any pesticide shown to cause cancer under any conditions must not be permitted in food.]

7. Environmental Monitoring

The Federal Government operates the *National Pesticides Monitoring Program* (NPMP) to (a) monitor baseline levels of pesticides in food, feed, man, soil, water, wildlife, fish and estuaries, and (b) study any developing trends (Ref. 53). Recently, responsibility for supervising and coordinating the NPMP activities has been vested with the EPA, although much of the actual monitoring work is performed under contract by the U.S. Geological Survey (USGS), the FDA, and others, including State agencies.

Overall guidance and evaluation of the NPMP rests with the *Federal Working Group on Pest Management* (FWGPM) consisting of members from the EPA and the following U.S. Departments: Agriculture; Commerce; Defense; the Interior; Health, Education and Welfare; State; and Transportation. The FWGPM is responsible to the Council on Environmental Quality (Executive Office of the President) and it is further subdivided into the *Monitoring Panel* with representatives from the Agricultural Research Service, Consumer and Marketing Service, Extension Service, Forest Service, Defense Department, Fish and Wildlife Service, USGS, FDA, EPA, National Marine Fisheries Service, National Science Foundation, and Tennessee Valley Authority.

The FWGPM sponsors a quarterly, *Pesticides Monitoring Journal*, published by the EPA to present and discuss data primarily from the pesticides monitoring network. Data from other sources are also accepted in appropriate format.

Table 8. Pesticides: 48-hour TLm values from static bioassay in μg/l: exceptions noted (from Ref. 10).

Insecticides

Pesticide	Stream invertebrate [1] Species	TLm	Cladocerans [2] Species	TLm	Fish [3] Species	TLm	Gammarus lacustris,[4] TLm
Abate	Pteronarcys californica.	100	------	------	Brook trout	1,500	640
Aldrin [5]	P. californica	8	Daphnia pulex.	28	Rainbow trout.	3	12,000
Allethrin	P. californica	28	D. pulex	21	do	19	20
Azodrin	------	------	------	------	do	7,000	------
Aramite	------	------	D. magna	345	Bluegill	35	100
Baygon [5]	P. californica	110	------	------	Fathead	25	50
Baytex [5]	P. californica	130	Simocephalus serrulatus.	3.1	Brown t.	80	70
Benzene hexachloride (lindane).	P. californica	8	D. pulex	460	Rainbow t.	18	88
Bidrin	P. californica	1,900	D. pulex	600	do	8,000	790
Carbaryl (sevin)	P. californica	1.3	D. pulex	6.4	Brown t.	1,500	22
Carbophenothion (trithion).	------	------	D. magna	0.009	Bluegill	225	28
Chlordane [5]	P. californica	55	S. serrulatus	20	Rainbow t.	10	80
Chlorobenzilate	------	------	S. serrulatus	550	do	710	------
Chlorthion	------	------	D. magna	4.5	------	------	------
Coumaphos	------	------	D. magna	1	------	------	0.14
Cryolite	------	------	D. pulex	5,000	Rainbow t.	47,000	------
Cyclethrin	------	------	D. magna	55	------	------	------
DDD (TDE) [5]	P. californica	1,100	D. pulex	3.2	Rainbow t.	9	1.8
DDT [5]	P. californica	19	D. pulex	0.36	Bass	2.1	2.1
Delnav (dioxathion)	------	------	------	------	Bluegill	14	690
Delmeton (systex)	------	------	------	14	do	81	------
Diazinon [5]	P. californica	60	D. pulex	0.9	do	30	500
Dibrom (naled)	P. californica	16	D. pulex	3.5	Brook t.	78	160
Dieldrin [5]	P. californica	1.3	D. pulex	240	Bluegill	3.4	1,000
Dilan	------	------	D. magna	21	do	16	600
Dimethoate (cygon).	P. californica	140	D. magna	2,500	do	9,600	400
Dimethrin	------	------	------	------	Rainbow t.	700	------
Dichlorvos [5] (DDVP)	P. californica	10	D. pulex	0.07	Bluegill	700	1
Disulfoten (di-syston)	P. californica	18	------	------	do	40	70
Dursban	Peteronareella badia	1.8	------	------	Rainbow t.	20	0.4
Endosulfan (thiodan)	P. californica	5.6	D. magna	240	do	1.2	64
Endrin [5]	P. californica	0.8	D. pulex	20	Bluegill	0.2	4.7
EPH	------	------	D. magna	0.1	do	17	36
Ethion	P. californica	14	D. magna	0.01	do	230	3.2
Ethyl guthion [5]	------	------	D. pulex	------	Rainbow t.	------	------
Fenthion	P. californica	39	D. pulex	4	------	------	------
Guthion [5]	P. californica	8	D. magna	0.2	Rainbow t.	10	0.3
Heptachlor [5]	P. badia	4	D. pulex	42	do	9	100
Kelthane (dicofel)	P. californica	3,000	D. magna	390	do	100	------
Kepone	------	------	------	------	do	37.5	------
Malathion [5]	P. badia	6	D. pulex	1.8	Brook t.	19.5	1.8
Methoxychlor [7]	P. californica	8	D. pulex	0.8	Rainbow t.	7.2	1.3
Methyl parathion [5]	------	------	D. magna	4.8	Bluegill	8,000	------
Morestan	P. californica	40	------	------	do	96	------
Ovex	P. californica	1,500	------	------	do	700	------
Paradichlorobenzene	------	------	------	------	Rainbow t.	880	------
Parathion [5]	P. californica	11	D. pulex	0.4	Bluegill	47	6
Perthane	------	------	D. magna	9.4	Rainbow t.	7	------
Phosdrin [5]	P. californica	9	D. pulex	0.16	do	17	310
Phosphamidon	P. californica	460	D. magna	4	do	8,000	3.8
Pyrethrins	P. californica	64	D. pulex	25	do	54	18
Rotenone	P. californica	900	D. pulex	10	Bluegill	22	350
Strobane [5]	P. californica	7	------	------	Rainbow t.	2.5	------
Tetradifon (tedion)	------	------	------	------	Bluegill	1,100	140
TEPP [5]	------	------	------	------	Fathead	390	52
Thanite	------	------	D. magna	450	------	------	------
Thimet	------	------	------	------	Bluegill	5.5	70
Toxaphene [5]	P. californica	7	D. pulex	15	Rainbow t.	2.8	70
Trichlorofon (dipterex).[5]	P. badia	22	D. magna	8.1	do	160	60
Zectran	P. californica	16	D. pulex	10	do	8,000	76

Table 8 cont'd

Herbicides, Fungicides, Defoliants, Algicides

Pesticide	Stream invertebrate[1]		Cladocerans[2]		Fish[3]		Gammarus lacustris,[4]
	Species	TL_m	Species	TL_m	Species	TL_m	TL_m
Ametryne	------	------	------	------	Rainbow t.	3,400	------
Aminotriazole	------	------	------	------	------	------	------
Aquathol	------	------	------	------	Bluegill	257	------
Atrazine	------	------	Daphnia magna.	3,600	Rainbow t.	12,600	------
Azide, potassium	------	------	------	------	Bluegill	1,400	10,000
Azide, sodium	------	------	------	------	do	980	9,000
Copper chloride	------	------	------	------	do	1,100	------
Copper sulfate	------	------	------	------	do	150	------
Dichlobenil	Pteronarcys californica.	44,000	Daphnia pulex.	3,700	do	20,000	1,500
2,4-D, PGBEE	------	------	D. pulex	3,200	Rainbow t.	960	1,800
2,4-D, BEE	P. californica	1,800	------	------	Bluegill	2,100	760
2,4-D, isopropyl	------	------	------	------	do	800	------
2,4-D, butyl ester	------	------	------	------	do	1,300	------
2,4-D, butyl + isopropyl ester.	------	------	------	------	do	1,500	------
2,4,5-T isooctyl ester	------	------	------	------	do	16,700	------
2,4,5-T isopropyl ester	------	------	------	------	do	1,700	------
2,4,5-T PGBE	------	------	------	------	do	560	------
2(2,4-DP) BEE	------	------	------	------	do	1,100	------
Dalapon	P. californica Very low toxicity	------	D. magna	6,000		Very Low toxicity.	
Dead-X	P. californica	5,000	D. pulex	3,700	Rainbow t.	9,400	5,600
DEF	P. californica	2,300	------	------	Bluegill	36	230
Dexon	P. californica	42,000	------	------	Bluegill	23,000	6,000
Dicamba	------	------	------	------	non-tox.	------	5,800
Dichlone	------	------	D. magna	26	Rainbow t.	48	11,500
Difolitan	P. californica	150	------	------	Channel Cat.	31	6,500
Dinitrocresol	P. californica	560	------	------	Rainbow t.	210	------
Diquat	------	------	------	------	do	12,300	------
Diuron	P. californica	2,800	D. pulex	1,400	do	4,300	380
Du-ter	------	------	------	------	Bluegill	33	------
Dyrene	------	------	D. magna	490	------	15	------
Endothal, copper	------	------	------	------	Rainbow t.	290	------
Endothal, dimethylamine.	------	------	------	------	do	1,150	------
Fenac, acid	P. californica	70,000	------	------	do	16,500	------
Fenac, sodium	P. californica	80,000	D. pulex	4,500	do	7,500	18,000
Hydram (molinate)	P. californica	3,500	------	------	do	290	------
Hydrothol 191	------	------	------	------	do	690	1,000
Lanstan (korax)	------	------	------	------	do	100	5,500
LFN	------	------	------	------	do	79	------
Paraquat	P. californica Very low toxicity	------	D. pulex	3,700	Very low toxicity.	------	18,000
Propazine	------	------	------	------	Rainbow t.	7,800	------
Silvex, PGBEE	------	------	D. pulex	2,000	do	650	------
Silvex, isoctyl	------	------	------	------	Bluegill	1,400	------
Silvex, BEE	------	------	------	------	do	1,200	------
Simazine	P. californica	50,000	------	------	Rainbow t.	5,000	21,000
Sodium arsenite	P. californica Very low toxicity	------	Simocephalus serrulatus.	1,400	do	36,500	------
Tordon (picloram)	------	------	------	------	do	2,500	48,000
Trifuralin	P. californica	4,200	D. pulex	240	do	11	5,600
Vernam (vernolate)	------	------	------	------	do	5,900	25,000

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[1] Stonefly bioassay was done at Denver, Colo., and at Salt Lake City, Utah. Denver tests were in soft water (35 mg/l TDS), non-aerated, 60 F. Salt Lake City tests were in hard water (150 mg/l TDS), aerated, 48–50 F. Response was death.

[2] **Daphnia pulex** and **Simocephalus serrulatus** bioassay was done at Denver, Colo., in soft water (35 mg/l TDS), non-aerated, 60 F. **Daphnia magna** bioassay was done at Pennsylvania State University in hard water (146 mg/l TDS), non-aerated, 68 F. Response was immobilization.

[3] Fish bioassay was done at Denver, Colo., and at Rome, N.Y. Denver tests were with 2-inch fish in soft water (35 mg/l TDS), non-aerated; trout at 55 F; other species at 65 F. Rome tests were with 2–2½-inch fish in soft water (6 mg/l TA: pH 5.85–6.4), 60 F. Response was death.

[4] **Gammarus** bioassay was done at Denver, Colo., in soft water (35 mg/l TDS), non-aerated, 60 F. Response was death.

[5] Becomes bound to soil when used according to directions, but highly toxic (reflected in numbers) when added directly to water.

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PESTICIDES IN WATER

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U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
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Pesticides in Surface Waters of the United States—a 5-Year Summary, 1964-68[1]

James J. Lichtenberg, James W. Eichelberger, Ronald C. Dressman, and James E. Longbottom

ABSTRACT

This report summarizes the results of five annual synoptic surveys (1964-68) for chlorinated hydrocarbon pesticides in surface waters of the United States. The results showed widespread occurrence of these compounds. The number of occurrences reached a peak in 1966 and then declined sharply in 1967 and 1968. Dieldrin and DDT and its congeners DDE and DDD were the compounds most frequently detected throughout the 5-year period. The maximum concentrations found have not exceeded permissible limits as they relate to human intake directly from a domestic water supply. However, they have often exceeded the environmental limit of 0.050 μg/liter recommended by the Federal Committee on Water Quality Criteria.

Introduction

Since September 1964, the Federal Water Quality Administration has conducted annual synoptic surveys for chlorinated hydrocarbon pesticides in surface waters (*1,2,3*). In September 1967 the fourth such survey was conducted, and in June 1968, the first spring survey was made. This surveillance activity has been a part of a continuing program for determining refractory organic substances in surface waters. The purpose is to provide information on present levels and trends of pesticides in waters to permit pollution control authorities to assess the degree of hazard and, if necessary, to provide the required control.

Through 1967 the surveys were conducted in September when streamflows are minimal. The 1968 survey was conducted in June in an effort to obtain comparative data during runoff periods after pesticide application.

Previous reports (*2,3*) have compared synoptic grab sample data with data obtained by the carbon adsorption method (CAM). Generally good agreement was noted between the two types of samples, and no further comparisons are reported here.

Samples were collected through the cooperative efforts of Federal, State, local, and private agencies at approximately 100 sampling stations. These stations are located mainly on interstate and international boundary waters at locations ranging from water treatment plant intakes to sites near mouths of rivers as they discharge to tidal waters.

This report summarizes the data obtained throughout the 5 surveys with emphasis on the 1967 and 1968 surveys. The number of samples analyzed for these surveys was 110 and 114, respectively. A total of 529 samples were analyzed for the 5 surveys.

Methods

The basic procedures for determination of chlorinated hydrocarbon pesticides are detailed in U.S. Department of the Interior Publication WP-22 (*4*) and in the "FWPCA Method for Chlorinated Hydrocarbon Pesticides in Water and Wastewater" (*5*). The samples were collected in 1-quart glass bottles (two per sample) equipped with screw caps fitted with Teflon liners. The samples were subjected to liquid-liquid extraction with 15% ethyl ether in hexane, dried over anhydrous sodium sulfate and concentrated to approximately 5 ml in a Kuderna-Danish evaporator. The extracts were carefully evaporated to 0.5 ml in a warm water bath, and up to 10 μl was injected into an electron capture gas chromatograph. If no response was obtained, the extracts were further concentrated to a maximum of

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[1] From the Analytical Quality Control Laboratory, Federal Water Quality Administration, U.S. Department of the Interior, 1014 Broadway, Cincinnati, Ohio 45202.

0.2 ml and again injected into the chromatograph. Those samples producing a response were then subjected to thin-layer chromatographic separation. The eluates from the thin layer were concentrated as before and again injected into the chromatograph.

The results were confirmed by multiple gas chromatographic analyses of the thin-layer eluates using the following conditions:

(1) A Perkin-Elmer Model 880 equipped with a parallel plate electron capture detector, an aluminum column 6′ x ¼″ O.D. packed with Gas-Chrom Q (60/80 mesh) coated with 5% QF-1 and 3% Dow-200, and a nitrogen carrier flow of 100 ml/minute. Temperatures were: injection port—250 C, column oven—185 C, and detector—205 C.

(2) A MicroTek Model 179 equipped with a Ni^{63} detector, an aluminum column 6′ x ¼″ O.D. packed with Gas Chrom Q (60/80 mesh) coated with 5% OV-17, and a nitrogen carrier flow of 100 ml/minute. Temperatures were: injection port—250 C, column oven—205 C, and detector—360 C.

(3) A MicroTek Model 179 equipped with a flame photometric detector, a glass column 4′ x 4 mm I.D. packed with Gas Chrom Q (60/80 mesh) coated with 2% Reoplex-400, and a carrier flow of 75 ml/minute. Temperatures were: injection port—185 C, column oven—185 C, and detector—160 C.

When the quantity of pesticide in the sample permitted, further confirmation was obtained using a microcoulometric gas chromatograph under conditions similar to (2) above; in which case, a lack of response for thiophosphate pesticides was considered as supporting evidence for their presence. Similarly, lack of response to the flame photometric detector supported the identification of the organochlorine pesticides.

Recovery data were obtained by dosing distilled water samples with the pesticides and carrying them through the entire analytical procedure. Recovery of organochlorine pesticides ranged from 65%-97% when samples were dosed at levels of 25-100 ng/liter. Recoveries of thiophosphate pesticides ranged from 40%-75% at dosages of 50-500 ng/liter. Every tenth sample was run in duplicate. Where results differed, the higher value was reported.

The methods are specific for dieldrin, endrin, DDT, DDE, DDD, aldrin, heptachlor, heptachlor epoxide, lindane, BHC, γ-chlordane, and technical chlordane. In addition, the use of the flame photometric detector provided specificity for many organophosphorus pesticides. For the 1967 and 1968 surveys, samples were also analyzed for methyl parathion, parathion, fenthion, ethion, malathion, and carbophenothion.

The practical lower limit of detectability for the chlorinated pesticides is 0.001 to 0.002 μg/liter, except for technical chlordane which has a limit of 0.005 μg/liter. Toxaphene can be detected, if it is present, at levels of the order of 1 μg/liter. The detection limits for the phosphorus compounds are 0.010 to 0.025 μg/liter. All results are reported without correction for recovery efficiencies. Thus, the reported concentrations represent minimum values, the actual value being equal to or greater than the reported value.

Results and Discussion

The results of the 1967 and 1968 surveys are listed in Tables 1 and 2. Table 3 lists the total number of samples and positive pesticide occurrences for each of the five surveys. The data show that the total occurrences peaked in 1966 and fell off significantly in 1967 and 1968. Fig. 1 summarizes the percent occurrences of 10 pesticides for the 5 surveys. It shows that the occurrences decreased sharply after 1966 for all pesticides except BHC, which showed only a slight decline. It also shows that the 1966 peak in total occurrences (Table 3) is largely due to the increase in DDD occurrences. The spring survey showed a slight increase in dieldrin and DDT.

Fig. 2 shows the geographical occurrence of dieldrin, the DDT group, and BHC for 1967 and 1968. Table 4 summarizes the occurrences (1964-68) by FWQA region. In 1966, the number of occurrences peaked in the South Central Region and in all regions east of the Mississippi. The Missouri Basin Region showed a gradual decline from 1964-1966, then a very sharp drop in 1967 and 1968. In the Southwest and Northwest Regions the occurrences fluctuated from 1964-1966 and then fell off to virtually nothing in 1967 and 1968. Throughout the 5 surveys dieldrin dominated the pesticide occurrences in all regions and in total occurrences with 199 positive results. DDT was second in overall occurrences with 86. DDT and its congeners DDE and DDD as a group accounted for 183 occurrences. Aldrin and chlordane were low with just two and five occurrences, respectively. Consistent geographical relationships among the various pesticides are difficult to identify; however, the overall occurrences show that dieldrin was slightly predominant in all regions east of the Mississippi and the DDT group, considered as one, was predominant in regions west of the Mississippi.

Since 1966, BHC has been detected in 10 of 12 samples from the main stem of the Ohio River. This consistent occurrence was verified by the results of the analyses of monthly CAM samples performed in this laboratory. The synoptic surveys and additional investigations by this laboratory produced only one positive result for BHC in eight major tributaries to the Ohio. That one was at Pittsburgh on the Allegheny River in September 1966. Twenty-three other BHC occurrences were widely scattered throughout the Country.

Endrin was found in over 30% of the samples in 1964; the reduction of endrin occurrences to zero in 1968 is particularly significant in light of its association with major fish kills in the Lower Mississippi prior to 1964.

Heptachlor was found in 14% of the samples in 1965 and in less than 1% thereafter. Heptachlor epoxide was found in approximately 14% of the samples in 1965 and 1966 and dropped to zero thereafter.

The 10 locations at which the highest levels of each pesticide were observed for each survey are listed in Table 5. Individual locations varied considerably. However, 2 stations on the Savannah River, at North Augusta, S. C. and Port Wentworth, Ga., were in the top 10 locations for dieldrin occurrences for all 5 surveys. Other rivers and locations that were consistently in the top 10 are the Merrimack, Schuylkill, Connecticut, Delaware, Potomac, Lower Ohio, Lower Mississippi, Missouri (at Kansas City), Rio Grande, and Red River (North).

The highest level of each pesticide found is listed in Table 6 along with water quality criteria for public water supplies and farmstead uses (6) and suggested maximum reasonable stream allowance (7). While the maximum concentrations have not exceeded permissible limits as they relate to human intake directly from a domestic water supply, they have in some cases exceeded or come quite close to the maximum reasonable allowance suggested by Ettinger and Mount (7). Because of the biological concentration factor, these levels are considered hazardous in waters from which fish are harvested for human consumption. In addition, because of their toxicity to fish, the Federal Committee on Water Quality Criteria recommends that environmental levels of these substances not be permitted to rise above 0.050 μg/liter (6).

Of the 84 stations where samples were collected in all 5 surveys, 12 had at least 1 positive occurrence in each survey. These are listed in Table 7. All but one of these are east of the Mississippi River. In addition, 16 widely spread locations had at least 1 positive occurrence in 4 of the 5 surveys.

Since pesticides are so common in surface waters, it is of interest to note those locations at which they are absent or occur infrequently. Table 8 lists the Stations that fall in this category. Locations in the west and northwest dominate this group.

Spring runoff after pesticide application was expected to cause an increase in the number of occurrences and in concentration levels in agricultural areas. Such an increase was not evident from the data obtained. This may be, in part, due to the wet spring experienced in much of the Country in 1968 which delayed planting and subsequent pesticide application in many areas. As a result, our collection period may have been too early to catch an increased pesticide load.

FIGURE 1.—*Percent occurrence of ten chlorinated hydrocarbon pesticides, 1964-68*

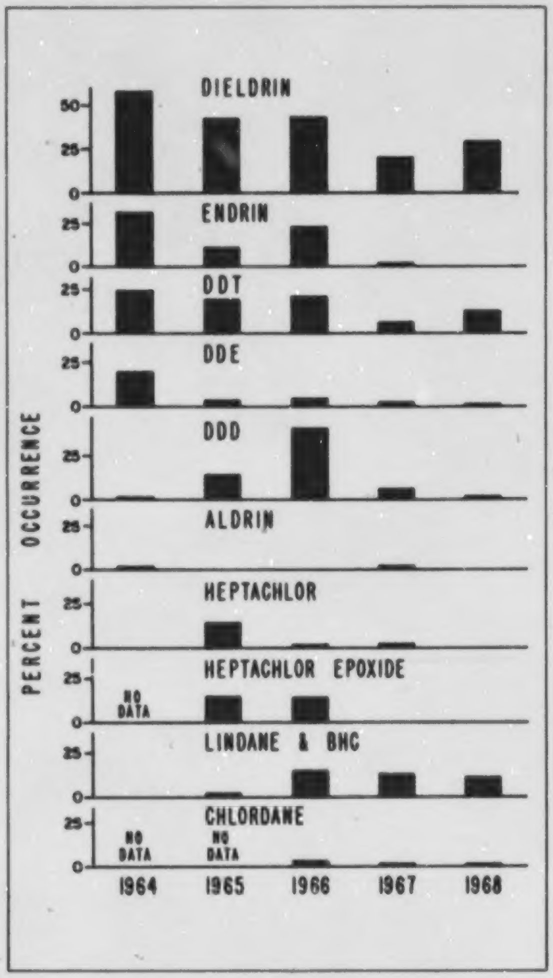

FIGURE 2.—*Occurrence of chlorinated hydrocarbon pesticides in surface waters, synoptic surveys of 1967 and 1968. (●—present; o—not detected)*

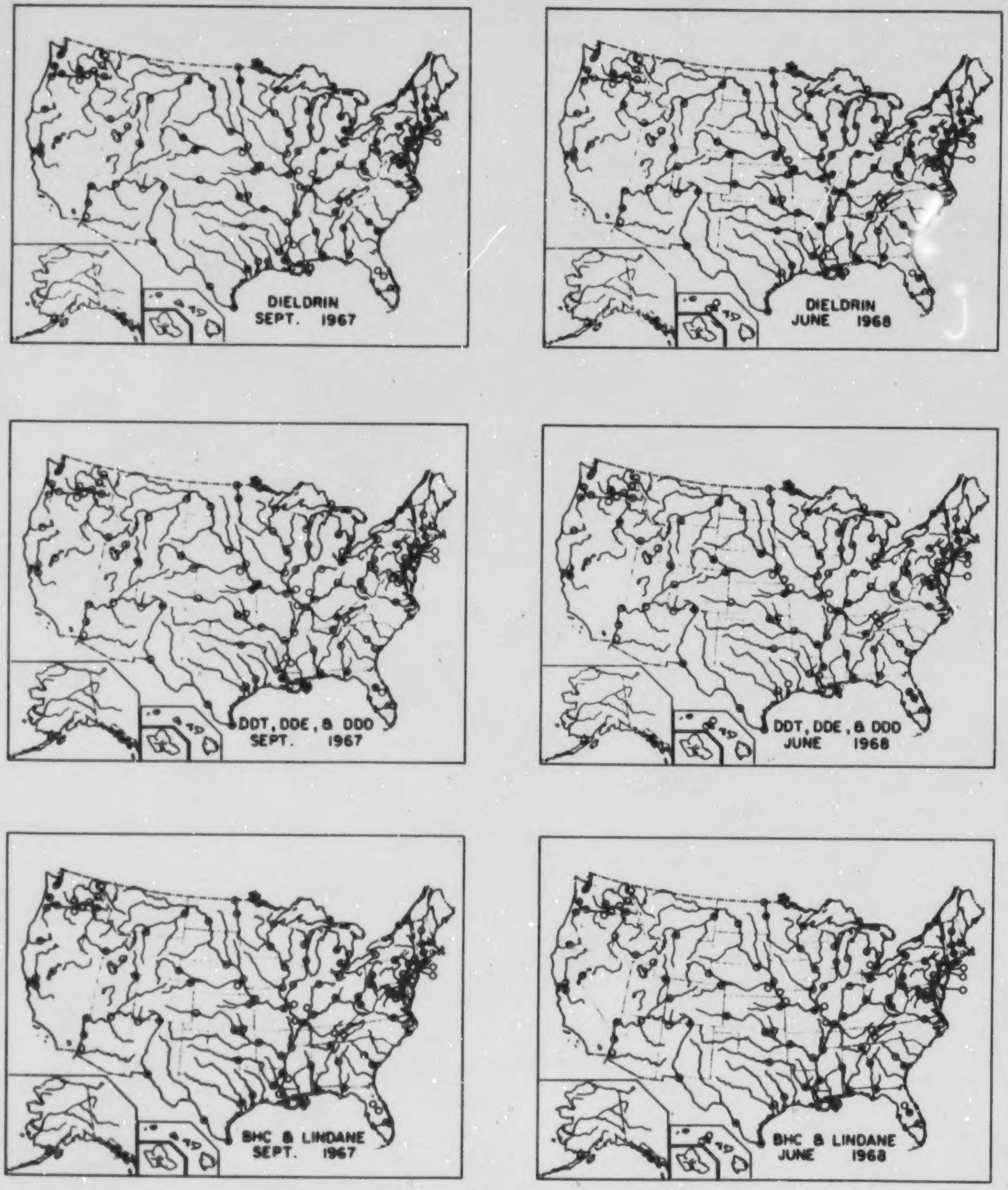
DIELDRIN
SEPT. 1967
DIELDRIN
JUNE 1968
DDT, DDE, & DDD
SEPT. 1967
DDT, DDE, & DDD
JUNE 1968
BHC & LINDANE
SEPT. 1967
BHC & LINDANE
JUNE 1968

TABLE 1.—*Results of synoptic survey for pesticides in surface waters, September 1967*

Location	Concentration in µg/liter [1]						
	Dieldrin	Endrin	DDT	DDE	DDD	Lindane	BHC
NORTHEAST REGION							
Connecticut River							
Enfield Dam, Conn.	.005	—	—	—	—	—	—
Northfield, Mass.	.017	—	—	—	—	.002	—
Wilder, Vt.	—	—	—	—	—	—	—
Schuylkill River							
Philadelphia, Pa.	.044	—	—	—	—	—	—
Hudson River							
Poughkeepsie, N.Y.	—	—	—	—	—	—	—
Narrows, N.Y.	—	—	—	—	—	—	—
Merrimack River							
Lowell, Mass.	.066	—	—	—	—	—	—
Delaware River							
Trenton, N.J.	.010	—	.017	—	.036	—	—
Martins Creek, Pa.	.013	—	—	—	—	.002	—
Raritan River							
Perth Amboy, N.J.	—	—	—	—	—	—	—
Delaware Bay							
a	—	—	—	—	—	—	—
b	—	—	—	—	—	—	—
MIDDLE ATLANTIC REGION							
Potomac River							
Great Falls, Md.	—	—	—	—	—	—	—
Washington, D.C.	.025	—	—	—	—	—	—
Shenandoah River							
Berryville, Va.	—	—	—	—	—	—	.002
Susquehanna River							
Conowingo, Md.	—	—	—	—	—	—	—
Sayre, Pa.	—	—	—	—	—	—	—
Roanoke, River							
John H. Kerr Dam, Va.	—	—	—	—	—	—	—
Neuse River							
Raleigh, N.C.	—	—	—	—	—	—	—
SOUTHEAST REGION							
Apalachicola River							
Chattahoochee, Fla.	.015	—	—	—	.053	.003	—
Beauclair River							
Lake Apopka, Fla.	—	—	.316	.050	.231	—	—
Escambia River							
Century, Fla.	—	—	—	—	—	—	—
Oklahawa River							
Orlando, Fla.	—	—	—	—	—	—	—
W. Palm Beach Canal							
W. Palm Beach, Fla.	—	—	—	—	—	.003	—
Chattahoochee River							
Lanett, Ala.	—	—	—	—	—	P	—
Savannah River							
Port Wentworth, Ga.	.039	—	—	—	—	—	—
North Augusta, S.C.	.087	—	—	—	—	—	—
Clinch River							
Kingston, Tenn.	.004	—	—	—	.032	—	—
Tennessee River							
Bridgeport, Ala.	—	—	—	—	—	—	—
Lenoir City, Tenn.	—	—	—	—	—	—	—
Tombigbee River							
Columbus, Miss.	—	—	—	—	P	—	—
OHIO BASIN REGION							
Allegheny River							
Pittsburgh, Pa.	—	—	—	—	—	—	—
Kanawha River							
Winfield Dam, W. Va.	—	—	—	—	—	P	—
Monongahela River							
Pittsburgh, Pa.	—	—	—	—	—	—	—
Ohio River							
Cairo, Ill.	—	—	—	—	—	—	—
Evansville, Ind.	.020	—	—	—	—	—	.008
Cincinnati, Ohio	—	—	—	—	—	—	.013
Above Addison, Ohio	—	—	—	—	—	—	006
Wabash River							
Lafayette, Ind.	.009	—	—	—	—	—	—
New Harmony, Ind.	—	—	—	—	—	—	—

TABLE 1.—*Results of synoptic survey for pesticides in surface waters, September 1967*—Continued

Location	Concentration in µg/liter [1]						
	Dieldrin	Endrin	DDT	DDE	DDD	Lindane	BHC
GREAT LAKES REGION							
St. Lawrence River							
Massena, N.Y.	—	—	—	—	—	—	P
Lake Erie							
Buffalo, N.Y.	P	—	—	—	—	—	—
Detroit River							
Detroit, Mich.	.014	—	—	—	—	—	.002
St. Clair River							
Port Huron, Mich.	—	—	—	—	—	—	—
St. Mary's River							
Sault Ste. Marie, Mich.	.004	—	—	—	—	.003	—
Saginaw River							
Bay City, Mich.	P	—	—	—	—	—	.007
Lake Superior							
Duluth, Minn.	—	—	—	—	—	—	—
Lake Michigan							
Milwaukee, Wis.	—	—	—	—	—	—	—
Maumee River							
Toledo, Ohio	—	.086	—	—	.270	—	—
Illinois River							
Peoria, Ill.	—	—	—	—	—	—	—
Mississippi River							
Cape Girardeau, Mo.	—	—	—	—	—	—	—
E. St. Louis, Ill.	—	—	—	—	—	—	—
Burlington, Iowa	—	—	—	—	—	—	—
Dubuque, Iowa	—	—	—	—	—	—	—
St. Paul, Minn.	—	—	—	—	—	—	—
Fox River							
Green Bay, Wis.	—	—	—	—	—	—	—
MISSOURI BASIN REGION							
Missouri River							
St. Louis, Mo.	—	—	—	—	—	—	—
Kansas City, Kans.	.012	—	.066	—	—	.010	—
Omaha, Nebr.	—	—	—	—	—	—	—
Yankton, S.Dak.	—	—	—	—	—	—	—
Bismarck, N.Dak.	—	—	—	—	—	—	—
North Platte River							
Henry, Nebr.	—	—	—	—	—	—	—
Platte River							
Plattsmouth, Nebr.	—	—	—	—	—	—	—
South Platte River							
Julesburg, Colo.	.024	—	—	—	—	—	—
Yellowstone River							
Sidney, Mont.	—	—	—	—	—	—	—
Rainy River							
Baudette, Minn.	—	—	—	—	—	—	—
Red River (North)							
Grand Forks, N.Dak.	.087	—	.054	—	—	—	—
Emerson, Manitoba	P	—	—	—	—	—	—
Kansas River							
Lawrence, Kans.	--	.133	—	—	.840	—	—
Big Horn River							
Hardin, Mont.	—	—	—	—	—	—	—
SOUTH CENTRAL REGION							
Atchafalaya River							
Morgan City, La.	—	—	—	—	—	—	—
Arkansas River							
Pendleton Ferry, Ark.	—	—	—	—	—	P	—
Port Smith, Ark.	—	—	—	—	—	—	—
Ponca City, Okla.	—	—	—	—	—	—	—
Coolidge, Kans.	—	—	—	—	—	—	—
Brazos River							
Arcola, Tex.	.024	—	—	—	P	—	—

TABLE 1.—*Results of synoptic survey for pesticides in surface waters, September 1967*—Continued

LOCATION	CONCENTRATION IN µg/LITER[1]						
	DIELDRIN	ENDRIN	DDT	DDE	DDD	LINDANE	BHC
SOUTH CENTRAL REGION—Continued							
Mississippi River							
New Orleans, La.	—	—	.019	—	—	—	—
Vicksburg, Miss.	—	—	—	—	—	—	—
Delta, La.	—	—	—	—	—	.024	—
West Memphis, Ark.	—	—	—	—	—	—	—
New Roads, La.	.008	—	—	—	.015	—	—
Red River (South)							
Alexandria, La.	—	—	—	—	—	—	—
Denison, Tex.	—	—	—	—	—	—	—
Rio Grande River							
Brownsville, Tex.	.002	—	.018	.022	—	—	—
El Paso, Tex.	—	—	—	—	—	—	—
Alamosa, Colo.	—	—	—	—	—	—	—
Verdigris River							
Nowata, Okla.	—	—	—	—	—	.009	—
Trinity River							
Houston, Tex.	—	—	—	—	—	—	—
SOUTHWEST REGION							
Bear River							
Preston, Idaho	—	—	—	—	—	—	—
Colorado River							
Yuma, Ariz.	—	—	—	—	—	—	—
Parker Dam, Calif.	—	—	—	—	—	—	—
Boulder City, Nev.	—	—	—	—	—	—	—
Page, Ariz.	—	—	—	—	—	—	—
Green River							
Dutch John, Utah	—	—	—	—	—	—	—
Klamath River							
Keno, Oreg.	—	—	—	—	—	—	—
Sacramento River							
Greens Landing, Calif.	—	—	—	—	—	—	—
San Joaquin River							
Vernalis, Calif.	—	—	—	—	—	—	—
San Juan River							
Shiprock, N. Mex.	—	—	—	—	—	—	—
Truckee River							
Farad, Calif.	—	—	—	—	—	—	—
NORTHWEST REGION							
Clearwater River							
Lewiston, Idaho	—	—	—	—	—	—	—
Columbia River							
Clatskanie, Oreg.	.018	—	—	—	—	—	—
Bonneville Dam, Oreg.	—	—	—	—	—	—	—
McNary Dam, Oreg.	—	—	—	—	—	—	—
Pasco, Wash.	—	—	—	—	—	—	—
Pend Oreille River							
Albeni Falls, Idaho	—	—	—	—	—	—	—
Snake River							
Wawawai, Wash.	—	—	—	—	—	—	—
American Falls, Idaho	—	—	—	—	—	—	—
Spokane River							
Post Falls, Idaho	—	—	—	—	—	—	—
Willamette River							
Portland, Oreg.	—	—	—	—	—	—	—
Yakima River							
Richland, Wash.	—	—	—	—	—	—	—

[1] The Lanett, Ala. sample contained .036 µg/liter of chlordane (tech). The Nowata, Okla. sample contained .002 µg/liter of aldrin and .003 µg/liter of heptachlor. The Wawawai, Wash. sample contained .050 µg/liter of parathion and .380 µg/liter of ethion. All other samples gave negative results for aldrin, heptachlor, heptachlor epoxide, parathion, methyl parathion, fenthion, ethion, malathion, and carbophenothion.

NOTE: — = not detected.

P = presumptive. Data are reported as presumptive in instances where the results of chromatography were highly indicative but did not meet all requirements for positive identification and quantification.

TABLE 2.—*Results of synoptic survey for pesticides in surface waters, June 1968*

Location	Concentration in µg/liter[1]						
	Dieldrin	Endrin	DDT	DDE	DDD	Lindane	BHC
NORTHEAST REGION							
Connecticut River							
Enfield Dam, Conn.	—	—	—	—	—	—	—
Northfield, Mass.	.022	—	—	—	—	—	—
Wilder, Vt.	—	—	—	—	—	—	—
Schuylkill River							
Philadelphia, Pa.	.027	—	—	—	—	—	—
Hudson River							
Poughkeepsie, N.Y.	.013	—	—	—	—	—	—
Narrows, N.Y.	.004	—	.030	—	—	—	—
Merrimack River							
Lowell, Mass.	.012	—	—	—	—	—	—
Delaware River							
Trenton, N.J.	.007	—	—	—	—	—	—
Martins Creek, Pa.	.007	—	.015	—	—	—	—
Raritan River							
Perth Amboy, N.J.	—	—	—	—	—	—	—
Delaware Bay	—	—	—	—	—	—	—
MIDDLE ATLANTIC REGION							
Potomac River							
Great Falls, Md.	.007	—	—	—	—	—	—
Washington, D.C.	—	—	.033	—	—	—	—
Shenandoah River							
Berryville, Va.	—	—	—	—	—	—	—
Susquehanna River							
Conowingo, Md.	.007	—	—	—	—	—	—
Sayre, Pa.	—	—	—	—	—	—	.009
Roanoke, River							
John H. Kerr Dam, Va.	.010	—	—	—	—	—	—
Neuse River							
Raleigh, N.C.	—	—	—	—	—	—	—
SOUTHEAST REGION							
Apalachicola River							
Chattahoochee, Fla.	.027	—	—	—	—	—	—
Beauclair River							
Lake Apopka, Fla.	—	—	.220	.041	.156	—	—
Escambia River							
Century, Fla.	.006	—	—	—	—	—	—
Oklahawa River							
Orlando, Fla.	.004	—	.005	—	—	—	.015
W. Palm Beach Canal							
W. Palm Beach, Fla.	—	—	—	—	—	—	—
Chattahoochee River							
Lanett, Ala.	—	—	—	—	—	—	.025
Savannah River							
Port Wentworth, Ga.	.039	—	—	—	—	—	—
North Augusta, S.C.	.059	—	—	—	—	—	—
Tennessee River							
Bridgeport, Ala.	—	—	—	—	—	—	—
Lenoir City, Tenn.	—	—	—	—	—	—	—
Oak Ridge, Tenn.	—	—	—	—	—	—	—
Tombigbee River							
Columbus, Miss.	.407	—	—	—	—	—	—
OHIO BASIN REGION							
Allegheny River							
Pittsburgh, Pa.	—	—	—	—	—	—	—
Kanawha River							
Winfield, W.Va.	.154	—	—	—	—	—	—
Monongahela River							
Pittsburgh, Pa.	—	—	.051	—	—	—	—
Ohio River							
Cairo, Ill.	.005	—	—	—	—	—	.020
Evansville, Ind.	—	—	—	—	—	—	.055
Cincinnati, Ohio	.014	—	—	—	—	—	.028
Above Addison, Ohio	—	—	—	—	—	—	.112
Wabash River							
Lafayette, Ind.	.005	—	—	—	—	—	—

TABLE 2.—*Results of synoptic survey for pesticides in surface waters, June 1968*—Continued

LOCATION	CONCENTRATION IN µG/LITER 1						
	DIELDRIN	ENDRIN	DDT	DDE	DDD	LINDANE	BHC
GREAT LAKES REGION							
St. Lawrence River							
Massena, N.Y.	—	—	—	—	—	—	—
Lake Erie							
Buffalo, N.Y.	—	—	—	—	—	—	—
Detroit River							
Detroit, Mich.	—	—	—	—	—	—	—
Grand River							
Grand Haven, Mich.	—	—	—	—	—	—	—
St. Clair River							
Port Huron, Mich.	—	—	—	—	—	—	—
St. Mary's River							
Sault Ste. Marie, Mich.	—	—	—	—	—	—	—
Saginaw River							
Bay City, Mich.	—	—	—	—	—	—	—
Lake Superior							
Duluth, Minn.	—	—	—	—	—	—	—
Lake Michigan							
Milwaukee, Wis.	—	—	—	—	—	—	—
Maumee River							
Toledo, Ohio	—	—	—	—	—	—	—
Illinois River							
Peoria, Ill.	—	—	—	—	—	—	—
Mississippi River							
Cape Girardeau, Mo.	.014	—	—	—	—	—	—
E. St. Louis, Ill.	.011	—	—	—	—	—	—
Burlington, Iowa	.010	—	—	—	—	—	—
Dubuque, Iowa	—	—	—	—	—	—	—
St. Paul, Minn.	.011	—	—	—	—	—	—
Fox River							
Green Bay, Wis.	—	—	—	—	—	—	—
MISSOURI BASIN REGION							
Missouri River							
St. Louis, Mo.	.010	—	—	—	—	—	-
Kansas City, Kans.	.009	—	—	—	—	—	—
Omaha, Nebr.	—	—	—	—	—	—	—
Yankton, S. Dak.	—	—	.053	—	—	—	—
Bismarck, N. Dak.	—	—	—	—	—	—	—
St. Joseph, Mo.	—	—	—	—	—	—	—
North Platte River							
Henry, Nebr.	—	—	—	—	—	—	—
Platte River							
Plattsmouth, Nebr.	.005	—	—	—	—	—	—
South Platte River							
Julesburg, Colo.	—	—	—	—	—	—	—
Yellowstone River							
Sidney, Mont.	—	—	—	—	—	—	—
Rainy River							
Baudette, Minn.	—	—	.037	—	—	—	—
Red River (North)							
Grand Forks, N.Dak.	—	—	—	—	—	—	.027
Emerson, Manitoba	—	—	—	—	—	—	—
Kansas River							
Lawrence, Kans.	—	—	.008	—	—	.003	—
Big Horn River							
Hard..., Mont.	—	—	—	—	—	—	—
SOUTH CENTRAL REGION							
Atchafalaya River							
Morgan City, La.	.005	—	—	—	—	—	—
Arkansas River							
Pendleton Ferry, Ark.	.005	—	.037	—	—	—	—
Fort Smith, Ark.	—	—	—	—	—	—	—
Ponca City, Okla.	—	—	—	—	—	—	.013
Coolidge, Kans.	.009	—	—	—	—	—	.025
Brazos River							
Arcola, Tex.	—	—	—	—	—	—	—
Mississippi River							
New Orleans, La.	—	—	—	—	—	—	—
Vicksburg, Miss.	—	—	.109	—	—	.004	—
West Memphis, Ark.	—	—	—	—	—	—	.005
St. Francisville, La.	—	—	—	—	—	—	—

TABLE 2.—*Results of synoptic survey for pesticides in surface waters, June 1968*—Continued

LOCATION	CONCENTRATION IN µg/LITER [1]						
	DIELDRIN	ENDRIN	DDT	DDE	DDD	LINDANE	BHC
SOUTH CENTRAL REGION—Continued							
Red River (South)							
Alexandria, La.	—	—	—	—	—	—	—
Denison, Tex.	—	—	—	—	—	—	—
Rio Grande River							
Brownsville, Tex.	—	—	—	—	—	—	—
El Paso, Tex.	—	—	—	—	—	—	—
Alamosa, Colo.	—	—	.029	—	—	—	—
Verdigris River							
Nowata, Okla.	—	—	—	—	—	—	—
Trinity River							
Houston, Tex.	—	—	—	—	—	—	—
SOUTHWEST REGION							
Bear River							
Preston, Idaho	—	—	—	—	—	—	—
Colorado River							
Yuma, Ariz.	—	—	—	—	—	—	—
Parker Dam, Calif.	—	—	—	—	—	—	—
Boulder City, Nev.	—	—	—	—	—	—	—
Page, Ariz.	—	—	—	—	—	—	—
Loma, Colo.	—	—	—	—	—	—	—
Green River							
Dutch John, Utah	—	—	—	—	—	—	—
Klamath River							
Keno, Oreg.	—	—	—	—	—	—	—
Sacramento River							
Green's Landing, Calif.	—	—	—	—	—	—	—
San Joaquin River							
Vernalis, Calif.	—	—	.030	—	—	—	—
San Juan River							
Shiprock, N. Mex.	—	—	—	—	—	—	—
Truckee River							
Farad, Calif.	—	—	—	—	—	—	—
Kiikii Stream							
Oahu, Hawaii	—	—	—	—	—	—	—
Waikele Stream							
Oahu, Hawaii	—	—	—	—	—	—	—
NORTHWEST REGION							
Clearwater River							
Lewiston, Idaho	—	—	—	—	—	—	—
Columbia River							
Clatskanie, Oreg.	—	—	—	—	—	—	—
Bonneville Dam, Oreg.	—	—	—	—	—	—	—
McNary Dam, Oreg.	—	—	—	—	—	—	—
Pasco, Wash.	—	—	—	—	—	—	—
Pend Oreille River							
Albeni Falls, Idaho	—	—	—	—	—	—	—
Snake River							
Wawawai, Wash.	—	—	—	—	—	—	—
Payette, Idaho	.004	—	.015	—	—	—	—
American Falls, Idaho	—	—	—	—	—	—	—
Spokane River							
Post Falls, Idaho	—	—	—	—	—	—	—
Willamette River							
Portland, Oreg.	—	—	—	—	—	—	—
Yakima River							
Richland, Wash.	.006	—	.017	—	—	—	—

[1] The Lanett, Ala. sample contained .169 µg/liter of chlorane (tech). All samples gave negative results for aldrin, heptachlor, heptachlor epoxide, parathion, methyl parathion, fenthion, ethion, malathion, and carbophenothion.

NOTE: — = not detected.

TABLE 3.—*Total number of chlorinated pesticide occurrences*

Year	Number of Samples Collected	Number of Samples With Positive Occurrences	Total Number of Positive Occurrences
1964	97	73	130
1965	99	56	120
1966	109	80	177
1967	110	34	56
1968	114	48	63
Total	529	291	546

TABLE 4.—*Pesticide occurrences by FWQA Region, 1964-68*

Pesticide	Northeast	Middle Atlantic	Southeast	Ohio Basin	Great Lakes Basin	Missouri Basin	South Central	Southwest	Northwest	Total
Dieldrin	31	14	28	20	22	25	34	13	12	199
Endrin	4	4	9	2	7	13	19	5	4	67
DDT	6	4	10	9	2	18	18	10	9	86
DDE	2	1	3	1	4	6	4	5	3	29
DDD	10	6	10	4	10	10	10	4	4	68
Aldrin	0	0	0	0	0	0	1	1	0	2
Heptachlor	1	0	1	2	3	4	3	2	0	16
Heptachlor epoxide	2	2	3	3	7	6	3	2	1	29
Lindane	2	0	2	0	1	2	3	0	0	10
BHC	2	2	3	12	4	3	7	2	0	35
Chlordane	0	1	3	0	0	0	0	1	0	5
Total	60	34	72	53	60	87	102	45	33	546
No. of Samples	53	32	50	41	76	70	86	65	56	529

TABLE 5.—*Top 10 locations at which highest levels were observed*

Location	μg/liter	Location	μg/liter	Location	μg/liter	Location	μg/liter	Location	μg/liter
1964		1965		1966		1967		1968	
				DIELDRIN					
Savannah River N. Augusta, S. C.	0.118	Tombigbee River Columbus, Miss.	0.100	Merrimack River Lowell, Mass.	0.167	Savannah River N. Augusta, S. C.	0.087	Tombigbee River Columbus, Miss.	0.407
Merrimack River Lowell, Mass.	0.071	Merrimack River Lowell, Mass.	0.068	Savannah River N. Augusta, S. C.	0.110	Red River (North) Grand Forks, N. Dak.	0.087	Kanawha River Winfield Dam, W. Va.	0.154
Potomac River Great Falls, Md.	0.040	Savannah River N. Augusta, S. C.	0.051	Savannah River Port Wentworth, Ga.	0.048	Merrimack River Lowell, Mass.	0.066	Savannah River N. Augusta, S. C.	0.059
Schuylkill River Philadelphia, Pa.	0.032	Kanawha River Winfield Dam, W. Va.	0.045	Susquehanna River Conowingo, Md.	0.031	Schuylkill River Philadelphia, Pa.	0.044	Savannah River Port Wentworth, Ga.	0.039
Rio Grande El Paso, Tex.	0.032	Rio Grande River Alamosa, Colo.	0.029	Delaware Bay	0.025	Savannah River Port Wentworth, Ga.	0.039	Schuylkill River Philadelphia, Pa.	0.027
Platte River Plattsmouth, Nebr.	0.023	Tennessee River Lenoir City, Tenn.	0.028	Connecticut River Northfield, Mass.	0.017	Potomac River Washington, D. C.	0.025	Apalachicola River Chattahoochee, Fla.	0.027
Connecticut River Northfield, Mass.	0.022	Ohio River Cairo, Ill.	0.028	Connecticut River Endfield Dam, Conn.	0.016	South Platte River Julesburg, Colo.	0.024	Connecticut River Northfield, Mass.	0.022
Savannah River Port Wentworth, Ga.	0.020	Mississippi River Dubuque, Iowa	0.024	Schuylkill River Philadelphia, Pa.	0.015	Brazos River Arcola, Tex.	0.024	Ohio River Cincinnati, Ohio	0.014
Mississippi River Vicksburg, Miss.	0.017	Missouri River Kansas City, Kans.	0.023	Chattahoochee River Lanett, Ala.	0.015	Ohio River Evansville, Ind.	0.020	Mississippi River Cape Girardeau, Md.	0.014
Mississippi River New Roads, La.	0.016	Savannah River Port Wentworth, Ga.	0.022	Kanawha River Winfield Dan, W. Va.	0.015	Columbia River Clatskanie, Oreg.	0.018	Hudson River Poughkeepsie, N. Y.	0.013
				ENDRIN					
Potomac River Great Falls, Md.	0.094	Mississippi River West Memphis, Ark.	0.116	Hudson River Narrows, N. Y.	0.069	Kansas River Lawrence, Kans.	0.133	NONE	
Rio Grande River El Paso, Tex.	0.067	Atchafalaya River Morgan City, La.	0.019	South Platte River Julesburg, Colo.	0.063	Maumee River Toledo, Ohio	0.086		
Big Horn River Hardin, Mont.	0.026	Delaware River Trenton, N. J.	0.018	Savannah River Port Wentworth, Ga.	0.031				
Mississippi River Vicksburg, Miss.	0.025	Tombigbee River Columbus, Miss.	0.015	St. Joseph River Benton Harbor, Mich.	0.029				
Connecticut River Northfield, Mass.	0.025	Clinch River Kingston, Tenn.	0.015	Lake Superior Duluth, Minn.	0.022				
Red River (North) Grand Forks, N. Dak.	0.023	Rio Grande River Alamosa, Colo.	0.014	Savannah River N. Augusta, S. C.	0.022				
Mississippi River New Roads, La.	0.023	Monongahela River Pittsburgh, Pa.	0.014	Bear River Preston, Idaho	0.019				
Yellowstone River Sidney, Mont.	0.021	Tennessee River Lenoir City, Tenn.	0.009	Clearwater River Lewiston, Idaho	0.015				
Columbia River Clatskanie, Oreg.	0.019	Red River (North) Grand Forks, N. Dak.	0.009	Connecticut River Northfield, Mass.	0.014				
Atchafalaya River Morgan City, La.	0.018	Mississippi River Delta, La.	0.008	Mississippi River Delta, La.	0.014				
				DDT					
Maumee River Toledo, Ohio	0.087	Rio Grande River Alamosa, Colo.	0.149	Brazos River Arcola, Tex.	0.123	Beauclair River Lake Apopka, Fla.	0.316	Beauclair River Lake Apopka, Fla.	0.220
Red River (North) Grand Forks, N. Dak.	0.072	San Juan River Shiprock, N. Mex.	0.125	Rio Grande River El Paso, Tex.	0.046	Missouri River Kansas City, Kans.	0.066	Mississippi River Vicksburg, Miss.	0.109
San Joaquin River Vernalis, Calif.	0.066	Colorado River Page, Ariz.	0.058	Mississippi River Vicksburg, Miss.	0.044	Red River (North) Grand Forks, N. Dak.	0.054	Missouri River Yankton, S. Dak.	0.053

TABLE 5.—*Top 10 locations at which highest levels were observed*—Continued

Location	µg/liter	Location	µg/liter	Location	µg/liter	Location	µg/liter	Location	µg/liter
1964		1965		1966		1967		1968	
				DDT—Continued					
Atchafalaya River Morgan City, La.	0.047	Platte River Plattsmouth, Nebr.	0.039	Arkansas River Fort Smith, Ark.	0.042	Mississippi River New Orleans, La.	0.019	Monongahela River Pittsburgh, Pa.	0.051
Mississippi River Vicksburg, Miss.	0.041	Spokane River Post Falls Dam, Idaho	0.037	Potomac River Great Falls, Md.	0.038	Rio Grande River Brownsville, Tex.	0.018	Rainy River Baudette, Minn.	0.037
Bear River Preston, Idaho	0.034	Red River (North) Grand Forks, N. Dak.	0.034	Mississippi River Delta, La.	0.031	Delaware River Trenton, N. J.	0.017	Arkansas River Pendleton Ferry, Ark.	0.037
Columbia River Clatskanie, Oreg.	0.034	Ohio River Cairo, Ill.	0.023	Missouri River Kansas City, Kans.	0.029			Potomac River Washington, D. C.	0.033
Red River (South) Alexandria, La.	0.031	South Platte River Julesburg, Colo.	0.023	Delaware River Trenton, N. J.	0.028			Hudson River Narrows, N. Y.	0.030
Willamette River Portland, Oreg.	0.029	Mississippi River Delta, La.	0.019	Lake Superior Duluth, Minn.	0.026			San Joaquin River Vernalis, Calif.	0.030
Apalachicola River Chattahoochee, Fla.	0.027	Mississippi River Vicksburg, Miss.	0.017	Snake River American Falls, Idaho	0.025			Rio Grande River Alamosa, Colo.	0.029
				DDE					
Maumee River Toledo, Ohio	0.015	San Juan River Shiprock, N. Mex.	0.009	Brazos River Arcola, Tex.	0.004	Beauclair River Lake Apopka, Fla.	0.050	Beauclair River Lake Apopka, Fla.	0.041
Bear River Preston, Idaho	0.011	Detroit River Detroit, Mich.	0.008	San Joaquin River Vernalis, Calif.	0.003	Rio Grande River Brownsville, Tex.	0.022		
Mississippi River St. Paul, Minn.	0.011	Yellowstone River Sidney, Mont.	0.002	St. Lawrence River Messena, N. Y.	0.002				
South Platte River Julesburg, Colo.	0.009	Platte River Plattsmouth, Nebr.	P	Columbia River Clatskanie,Oreg.	0.001				
Delaware River Martins Creek, Pa.	0.008	Rainy River Baudette, Minn.	P	Arkansas River Pendleton Ferry, Ark.	P				
Mississippi River West Memphis, Ark.	0.007			Red River (South) Alexandria, La.	P				
Columbia River Clatskanie, Oreg.	0.005			Rio Grande River El Paso, Tex.	P				
San Joaquin River Vernalis, Calif.	0.005			Lake Superior Duluth, Minn.	P				
Snake River Payette, Idaho	0.005			Hudson River Poughkeepsie, N. Y.	P				
Seven Stations	0.004			Hudson River Narrows, N. Y.	P				
				DDD					
Shenandoah River Berryville, Va.	0.083	Rio Grande River Brownsville, Tex.	0.026	Connecticut River Endfield Dam, Conn.	0.013	Kansas River Lawrence, Kans.	0.840	Beauclair River Lake Apopka, Fla.	0.156
All others	<0.075	Delaware River Trenton, N. J.	0.018	Rio Grande River Brownsville, Tex.	0.013	Maumee River Toledo, Ohio	0.270		
		Willamette River Portland, Oreg.	0.013	St. Joseph River Benton Harbor, Mich.	0.013	Beauclair River Lake Apopka, Fla.	0.231		
		Missouri River Kansas City, Kans.	0.011	Raritan River Perth Amboy, N. J.	0.012	Apalachicola River Chattahoochee, Fla.	0.053		
		St. Lawrence River Messena, N. Y.	0.010	Detroit River Grosse Isle, Mich.	0.012	Delaware River Trenton, N. J.	0.036		
		Platte River Plattsmouth, Nebr.	0.010	Potomac River Great Falls, Md.	0.012	Clinch River Kingston, Tenn.	0.032		

TABLE 5.—*Top 10 locations at which highest levels were observed*—Continued

LOCATION	µg/LITER	LOCATION	µg/LITER	LOCATION	µg/LITER	LOCATION	µg/LITER	LOCATION	µg/LITER
1964		1965		1966		1967		1968	
				DDD—Continued					
		Waikele Stream Oahu, Hawaii	0.008	Arkansas River Pendleton Ferry, Ark.	0.012	Mississippi River New Roads, La.	0.015		
		Red River (South) Alexandria, La.	0.008	Chattahoochee River Lanett, Ala.	0.011	Tombigbee River Columbus, Miss.	P		
		Merrimack River Lowell, Mass.	0.007	Atchafalaya River Morgan City, La.	0.010	Brazos River Arcola, Tex.	P		
		Potomac River Washington, D. C.	0.007	Missouri River Kansas City, Kans.	0.010				
				BHC					
Delaware River Martins Creek, Pa.	P	Red River (North) Grand Forks, N. Dak.	0.004	Ohio River Cincinnati, Ohio	0.056	Ohio River Cincinnati, Ohio	0.013	Ohio River Addison, Ohio	0.112
Mississippi River West Memphis, Ark.	P	Ohio River Cairo, Ill.	0.002	Hudson River Narrows, N. Y.	0.034	Ohio River Evansville, Ind.	0.008	Ohio River Evansville, Ind.	0.055
All others	<0.025	Verdigris River Nowata, Okla.	P	Ohio River Addison, Ohio	0.026	Saginaw River Bay City, Mich.	0.007	Ohio River Cincinnati, Ohio	0.028
		Connecticut River Endfield Dam, Conn.	P	Rio Grande River El Paso, Tex.	0.023	Ohio River Addison, Ohio	0.006	Red River (North) Grand Forks, N. Dak.	0.027
		Monongahela River Pittsburgh, Pa.	P	South Platte River Julesburg, Colo.	0.022	Shenandoah River Berryville, Va.	0.002	Chattahoochee River Lanett, Ala.	0.025
				Trinity River Livingston, Tex.	0.013	Detroit River Detroit, Mich.	0.002	Arkansas River Coolidge, Kans.	0.025
				Allegheny River Pittsburgh, Pa.	0.013	St. Lawrence River Massena, N. Y.	P	Ohio River Cairo, Ill.	0.020
				Mississippi River St. Paul, Minn.	0.012			Oklawaha River Orlando, Fla.	0.015
				Mississippi River Vicksburg, Miss.	0.010			Arkansas River Ponca City, Okla.	0.013
				San Joaquin River Vernalis, Calif.	0.008			Susquehanna River Sayre, Pa.	0.009
				Chattahoochee River Lanett, Ala.	0.008				
				Arkansas River Ponca City, Okla.	0.008				

P = presumptive. Data are reported as presumptive in instances where the results of chromatography were highly indicative but did not meet all requirements for positive identification and quantification.

TABLE 6.—*Maximum pesticide concentration found vs. permissible water supply criteria and reasonable stream allowance*
[blanks = criteria not given]
µg/LITER

Pesticide	Permissible Criteria [1]	Desirable Criteria [1]	Maximum Reasonable Stream Allowance [2]	Maximum Concentration Found
Dieldrin	17	absent	0.25	0.407
Endrin	1	do	0.1	0.133
DDT	42	do	0.5	0.316
DDE				0.050
DDD				0.840
Heptachlor	18	absent	1.0	0.048
Heptachlor epoxide	18	do	1.0	0.067
Aldrin	17	do	0.25	0.085
Lindane (BHC)	56	do	5.0	0.112
Chlordane	3	do	0.25	0.169
Methoxychlor	35	do	20.0	(3)
Toxaphene	5	do	2.5	(4)
Organophosphates plus Carbamates	100	do		0.380
Herbicides: 2,4-D plus 2,4,5-T and 2,4,5-TP	100	do		(3)
Phenols	1	do		(3)

[1] From the "Report of the Committee on Water Quality Criteria" (*6*)
[2] Suggested by Ettinger and Mount (*7*)
[3] Not determined
[4] Not detected

TABLE 7.—*Locations with high frequency of pesticide occurrence (at least one pesticide found in each survey)*

River	Location
Merrimack	Lowell, Mass.
Delaware	Trenton, N. J.
Delaware	Martins Creek, Pa.
Schuylkill	Philadelphia, Pa.
Potomac	Great Falls, Md.
Apalachicola	Chattahoochee, Fla.
Chattahoochee	Lanett, Ala.
Savannah	Port Wentworth, Ga.
Savannah	North Augusta, S. C.
Ohio	Evansville, Ind.
Ohio	Cincinnati, Ohio
Kansas	Lawrence, Kans.

TABLE 8.—*Locations with low frequency of pesticide occurrence*

River	Location	Surveys	Occurrences
Connecticut	Wilder, Vt.	5	1
Raritan	Perth Amboy, N. J.	3	1
Lake Erie	Buffalo, N. Y.	5	1
St. Clair	Port Huron, Mich.	4	0
Rainy	International Falls, Minn.	3	0
Colorado	Parker Dam, Ariz.-Calif.	5	0
Colorado	Boulder City, Nev.	5	1
Truckee	Farad, Calif.-Nev.	5	0
Green	Dutch John, Utah	5	0
Snake	American Falls, Utah	3	1
Pend Oreille	Albeni Falls, Idaho	5	0
Klamath	Keno, Oreg.	5	1
Columbia	McNary Dam, Oreg.	5	0
Columbia	Pasco, Wash.	5	1
Columbia	Bonneville, Oreg.	3	1

Summary and Conclusions

The occurrences of chlorinated hydrocarbon pesticides continue to be widespread. However, after reaching a peak in 1966, the total number of occurrences throughout the Country dropped sharply in 1967 and 1968. This trend is consistent with production and usage reports of the U.S. Department of Agriculture (*8*) and the U.S. Department of the Interior (*9*) which show a trend toward decreased use of the persistent chlorinated hydrocarbon compounds and an increase in the use of organophosphorus and carbamate compounds. The absence of a corresponding increase in the occurrences of organophosphates may be due to their relatively rapid hydrolysis rate in water and the method of analysis which was not designed specifically for this class of compounds.

The data reported here and the grab sample and CAM sample data reported earlier (*1,2,3*) represent pesticide levels and trends in the major interstate waterways sampled. They do not, necessarily, reflect the conditions existing in all sub-basins or areas of heavy pesticide use, such as irrigation districts. For example, in extensive surveillance operations conducted by FWQA in the Lower Colorado River area during the summers of 1967 and 1968, the occurrences were frequent and the levels generally higher for both chlorinated and organophosphorus pesticides *unpublished data.*

Dieldrin continued to dominate the pesticide occurrences, although the total number of occurrences had dropped significantly.

BHC has been found consistently in the main stem of the Ohio River since 1966. The source or sources of this material have not yet been determined.

The pesticide concentrations found were 1/10 to 1/500 of the permissible levels for water supplies given in Water Quality Criteria (*6*). However, in some instances the concentrations found have exceeded the suggested maximum reasonable stream allowance (*7*), as well as the environmental limit recommended by the Committee on Water Quality Criteria (*6*).

Future surveys should be conducted to determine if the decreasing trend of chlorinated hydrocarbon pesticides occurrences is continuing. The methods of analysis should include procedures specifically designed to determine organophosphorus compounds. A greatly expanded sampling program would be necessary to determine seasonal variations in pesticide occurrences. This could best be done on a regional basis.

See Appendix for chemical names of compounds mentioned in this paper.

Acknowledgments

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(7) *Ettinger, M. B. and D. I. Mount. 1967.* A wild fish should be safe to eat. Environ. Sci. Technol. 1:203-205.

(8) *U. S. Department of Agriculture, Agricultural Stabilization and Conservation Service. 1968.* The pesticide review—1968. ASCS-155. p. 38-43.

(9) *U. S. Department of the Interior, Federal Water Pollution Control Administration. Central Pacific Basins Project. 1967.* Effect of San Joaquin master drain on San Francisco Bay and Delta. p. 40-41.

B. PESTICIDE ANALYSIS

Much detailed information is available on pesticide residues in the environment, largely the result of highly sensitive analytical techniques developed specifically for pesticides. Standard and official procedures for the application of these techniques to monitoring pesticide residues in the aquatic environment may be found in the Federal Register (Ref. 1; see H2O-PES, App.2) and the following publications:

a) Standard Methods for the Examination of Water and Waste Water, 13th Edition, 1971 (Ref. 2).

b) The Identification and Measurement of Chlorinated Hydrocarbon Pesticides in Surface Waters, 1966 (Ref. 3).

c) Methods for Organic Pesticides in Water and Wastewater, 1971 (Ref. 4; a successor to Ref. 3).

d) Methods for Analysis of Organic Substances in Water, 1972 (Ref. 5).

The procedures described in the above "methods manuals" are those which have been carefully developed over a period of time by a number of qualified analysts and technicians. This assures greater simplicity and reliability which is so important for comparing levels of environmental contamination from laboratory to laboratory and region to region. The problem of monitoring contamination of the aquatic environment with pesticide residues is complex, among the most complex of all environmental pollution problems. As a result there is a continuing need for faster, more sensitive and comprehensive analytical procedures. Some of the latest techniques have become useful so quickly that the standard methods manuals (Ref. 2 to 5) do not include them. This is particularly true of combined or tandem gas chromatography-mass spectrometry (GC-MS) which can be computerized for a comprehensive analysis or made to search for specific pollutants (see section 9).

Review publications useful for keeping abreast of pesticide and pesticide residue analytical and methodological developments include:

a) "Pesticide Residues," biennially (odd years) in Analytical Reviews, Analytical Chemistry (Ref. 6).

b) Residue Reviews, F.A. Gunther, Ed. (Ref. 7).

c) Analytical Methods for Pesticides, Plant Growth Regulators, and Food Additives, G. Sweig, Ed. (Ref. 8).

Discussion and review of analytical techniques, sampling procedures, sample preparation and numerous incidental facets related to analysis of aquatic pesticide residues may be found in two chapters from monographs:

a) "Analysis for Pesticides and Herbicides in the Water Environment," by Faust and Suffet in Water and Water Pollution Handbook, Vol 3, (Ref. 9).

b) "Assay Procedures for Pesticide Residues," by Van Middelem in Pesticides in the Environment, Vol. 1, Part II (Ref. 10).

Early procedures and references for aquatic pesticide residue analysis were discussed breifly in Water Quality Criteria (Ref. 11).

1. Residue Analysis

The study of pesticides in the environment, particularly the aquatic environment, virtually always involves what has come to be known as residue analysis. Originally applied to pesticides remaining in foodstuffs, pesticide residues now have an environmental connotation as well. It is pertinent to note that the term "residues" also includes degradation and metabolic products derived from pesticides. Thus DDT residues include the summation of DDT itself and all of its significant and measurable products, such as DDE, DDD and others (see Fig. 1, part A).

Pesticide residue analysis differs so greatly from pesticide formulation analysis that the two should neither be considered comparable nor be contemplated in the same laboratory area. Formulation analysts work in the g/l or g/kg range, whereas the residue analyst must contend with samples in the mg/l or mg/kg range down to the ng/l or ng/kg level (Ref. 10). At such low levels laboratory equipment, glassware, solvents and reagents must be maintained scrupulously free of contamination either through rigorous cleaning or purification procedures (Ref. 3-5).

1.1 Analytical Sensitivity

Until the mid-1950's, pesticide residue analysis was confined largely to colorimetric methods, total chlorine, cholinesterase inhibition and bioassay (Ref. 10). Minimum detection levels were about 50 µg/l or µg/kg. With the development of gas chromatography (GC) and thin-layer chromatography (TLC), residue sensitivity increased more than 1000-fold. Currently GC detection sensitivity extends down to the nanogram and even picogram range (10^{-9} to 10^{-12} g), making parts per billion (ng/l) to parts per trillion (pg/l) detection feasible, *if* interferences can be excluded.

1.2 Aquatic Sample Sensitivity

Pesticide residue analysis is concerned with the lower limit of detection, i.e., the actual, reproducible, minimum detectable concentration for a given procedure (Ref. 9) as distinguished from sensitivity to pure standards. In various aquatic environments frequently this has been difficult to define unambiguously. It depends on the nature of the sample source. For example, water normally contains living organisms, suspended solids, dissolved minerals and organic matter. These materials drastically affect the state in which pesticides exist in water -- they may be adsorbed on solid particles or dissolved in fatty substances, and they form complexes or otherwise associate with organic materials.

Criteria vary according to sample type and laboratory skill. Holden and Marsden (Ref. 12) suggest a 0.5 ng/l minimum detection level for dieldrin in clean waters vs. 100 to 300 ng/l in domestic sewage effluents, whereas Epps *et al.*(Ref. 13) strove for a 1 μg/l minimum detection, but where interferences were great, concentrations less than 100 μg/l were not reported with confidence. Some suggested minimum detectable limits compiled from the literature (Ref. 9) are shown in Table 1.

Table 1
Suggested Detection Limits (μg/l) for Aquatic Pesticides According to Sample Size (from Ref. 9).

	3.8*l*	1*l*
BHC	0.005	---
Lindane	0.005	0.005
Heptachlor and/or heptachlor epoxide	0.010	0.005
Aldrin	0.010	0.005
Dieldrin	0.010	0.005
Endrin	0.020	0.005
Chlordane	0.040	---
Toxaphene	0.080	---
Strobane	0.080	---
DDT	0.020	0.010
DDD (TDE)	0.020	0.005
2,4-D	---	0.100
2,4,5-T	---	0.005
2(2,4,5-TP)	---	0.005

Statistical variability in the analytical technique is also important. Variance around a mean value influences the confidence with which minute levels of pesticides are reported (Ref. 9). There is also the variability among individual analysts and between laboratories. Careful, consistent sampling and analysis by trained personnel is essential.

2. Sampling

Several factors must be considered in sampling a surface water or bottom mud for subsequent pesticide analysis. It is vital to obtain and preserve a sample representative of the environment under study. Several years ago government pesticide residue analysts recommended the following procedure for aquatic samples, either a 1 or 4 liter grab sample (Ref. 14):

> "All samples are to be collected in glass bottles. Prior to collection, scrupulous cleansing of sample containers is required. Chromic acid cleaning solution or other suitable cleansing agents are to be used, followed by several rinsings with organic-free distilled water. Containers are to be further treated as necessary to destroy remaining traces of organic matter; heat treating of containers at 300°C has been found satisfactory. Bottles are to be stoppered immediately to prevent airborne contamination. The sample must have no contact with rubber, cork, and most plastics: Teflon, however, will not contaminate the sample. Rubber or cork stoppers may be used if wrapped carefully with a double layer of organic-free tinfoil or aluminum foil, taking care to avoid rupture of the foil when stoppering the bottle.
>
> "The sample is to be collected in the prepared glass bottle by lowering it in a weighted bottle holder in a vertical section of the stream which is representative of the stream cross section. The bottle is to be lowered as nearly as possible to the bottom of the stream and returned to the surface so that all points in the vertical section are represented in the sample."

If possible, the samples should be shipped in suitable packing cases for analysis within 2 days after collection; if not, they should be stored in a cool, dark place. Many of these recommendations were made for the relatively stable chlorinated hydrocarbon and phenoxyalkanoic acids. However, if the presence of organic phosphate, carbamate or urea is suspected, the analytical work should then proceed as quickly as possible because these pesticides may hydrolyze on standing. Detailed directions are given in the EPA manual (Ref. 4).

Losses of chlorinated hydrocarbons, especially DDT, may be serious in the collection and transportation of samples. Bowman *et al.*(Ref. 15) found that a high proportion of DDT was deposited on the inner walls of glass, aluminum or paper containers. Also, more than 50% of a 0.01 mg/l suspension of DDT in water volatilized within 24 hr. In their study of γ-BHC, *p,p'*-DDT, and dieldrin, Chiba and Morley (Ref. 16) found small cumulative losses in the filtration, partitioning, and washing steps.

2.1 Recovery Efficiency

Faust and Suffet report that it has been general practice to report recovery efficiencies as determined by techniques of fortification (standard addition), i.e., the addition of a known quantity of a pesticide to the sample prior to laboratory analysis to obtain a theoretical efficiency of the procedure (Ref. 9). Whether the recovery efficiencies from the fortification correspond to the actual recovery efficiencies from field samples is uncertain. For example, field samples are "weathered" (i.e., subject to physical, chemical, and metabolic transformations) and may exist in aggregates or in molecular form, in or on plant tissue, or soil, etc. Thus, the pesticide residue in field samples may not be in the same physical condition as the fortified sample. Recovery of the field sample is best determined by isotope tracers in the field pollutant. See Vol. 3 (RADIATION) for detection techniques.

3. Sample Extraction

Before the presence of pesticide residues can be identified and quantitated they must be removed from the surrounding sample matrix and isolated from serious analytical interferences. It is customary to extract a pesticide from water for analysis with an immiscible, volatile organic solvent which can be easily evaporated after extraction. Because of matrix variables, not all of a pesticide may be recovered. Extraction of pesticide trace residues (< μg/1) from public water supplies, some natural waters, and sewage treatment plant effluents may be relatively simple, involving only the carbon adsorption method (CAM) followed by preparation of a carbon chloroform extract (CCE) (see Ref. 3). Simple serial liquid extraction of a 1 to 4 liter sample may also suffice for pesticide residues down to the ng/1 level (Ref. 5).

Conversely, grossly polluted waters may contain many organic compounds which could interfere with later analysis; therefore, more elaborate extraction and cleanup procedures become necessary (Ref. 9, 10). The method of extraction and type of solvent(s) depends not only on the sample matrix, but the physical and chemical properties of the residues of interest and must be compatible with the final method of analysis (Ref. 10). For example, chlorinated hydrocarbon solvents (methylene chloride, chloroform, carbon tetrachloride) should be avoided with GC analysis by electron capture (see section 7.2.1). Standard methods manuals (Ref. 2-5) take a practical and sometimes brief approach to pesticide residue extractions; however, Faust and Suffet (Ref. 9) and Van Middelem (Ref. 10) discuss this in detail. Reference 9 deals more with aqueous samples, whereas Reference 10 emphasizes foodstuffs and other assorted mixed matrices, including plant and animal tissue, muds and sediments. It is beyond the scope of this survey to discuss all sample extraction aspects exhaustively; however, some highlights follow.

3.1 Carbon Adsorption Method (CAM)

Activated carbon has been used for extraction of organic pesticides from water as a continuous device in the field, and as a batch concentration and preliminary cleanup technique in the laboratory (Ref. 9). It offers two advantages: it is continuous and large water volumes can be sampled. There are, however, limitations:

a) The adsorption and subsequent extraction steps are not quantitative.

b) Microbial growth may occur on the surface.

c) Certain organics may be preferentially adsorbed according to carbon type, pH, temperature, and minerals in the water.

d) Organics with a high affinity for carbon may displace others.

e) Improper purification of the carbon can lead to high blanks.

f) Pesticides may decompose during the adsorption and desorption steps.

Alternative adsorbents and absorbents are under active investigation (Ref. 17).

3.2 Liquid-Liquid Extraction

In liquid-liquid extraction, a dissolved organic solute (i.e., the pesticide residue) is distributed preferentially between two immiscible solvents (e.g., hexane/water). Choice of solvent pairs to be employed frequently is based upon semiempirical knowledge about the polar-nonpolar character of the solute and each solvent, and solute-solvent interactions such as dipole or hydrogen bond interactions (Ref. 9). Once a suitable solvent is found, the analyst may employ either serial (stepwise, repetitive) or continuous extraction. Environmental factors such as pH, ionic strength, and temperature may require consideration. Decisions based on percentage of recovery data often are arbitrary and empirical, and recoveries may vary considerably (see Tables in Ref. 9).

Hydrocarbon solvents (hexane, benzene and petroleum ether) have found the widest use for recovery of chlorinated hydrocarbons from water by serial extraction. Extraction efficiencies, generally ⩾ 85%, can vary widely unless the number of serial extractions and the ratio of sample volume to solvent volume are standardized (Ref. 9). The solvent best for a particular organophosphate, a group of them, or an organophosphate and its degradation products is still not clear in most cases (Ref. 9). Proper pH is critical since organophosphates may hydrolyze under acidic or alkaline conditions. Chloroform and ether are preferred solvents for phenoxyalkanoic acid herbicides with pH adjustment to 2.0 (Ref. 9).

Liquid-liquid extraction suffers the following limitations with pesticide residues from natural waters (Ref. 9):

a) No single solvent can extract all organic pesticides.

b) Organic interferences are also coextracted from polluted waters, necessitating additional cleanup.

c) pH of the water sample must be correct.

d) Volatilization losses may occur during extraction and evaporation.

e) Recoveries may be incomplete if small particles are suspended in the aqueous phase.

On the other hand, recoveries are fairly good in most cases (⩾ 85%) and samples are readily prepared for the final analytical steps.

3.3 Solid Extraction

Pesticide residue extraction from solid or solid-liquid matrices such as filtered sediment, mud or animal tissue presents special problems which may require individually tailored procedures. Van Middelem (Ref. 10) cites a number of examples, particularly in samples of biological origin. Maceration with the extraction solvent(s) followed by centrifugation and/or filtration is a customary overall approach. The resultant extract usually requires cleanup prior to final identification and quantitative estimation. Reference 5 contains detailed methodology specifically for the extraction of bottom (sediment) samples.

4. Sample Cleanup

The term, "cleanup" refers to purification procedures employed to remove various extraneous substances from the sample which, if carried forward through the analysis, would interfere with the final determination of identity and quantity of pesticide(s) present. The type and extent of cleanup depends on the nature of the sample and the method of pesticide analysis. Seriously polluted waters, sediments, muds and tissues usually require greater cleanup than public water supplies, highly treated sewage plant effluents, and some natural waters.

Cleanup should be restricted to only that necessary since even the best cleanup methods may remove some pesticide. When evaluating a cleanup procedure, the recovery efficiency should be > 75-80% of the pesticide added prior to cleanup (Ref. 10). Percent recoveries of various levels of the pesticide in question should be determined and these levels should cover the range expected with actual samples.

As with the extraction of pesticide samples, there is no single, universal cleanup procedure applicable to all types of extracts. Most current methods involve partition, adsorption, or chemical methods, or a combination of these. Early reviews on cleanup procedures for pesticide residues in various biological extracts are given by Gunther (Ref. 18) and Thornburg (Ref. 19). Recent practice is discussed by Faust and Suffet (Ref. 9) and by Van Middelem (Ref. 10) more completely than can be covered in this survey. Some of the more important aspects follow.

4.1 Liquid Partition

Partition between immiscible (e.g., polar and non-polar) solvents to effect cleanup of interferences is a liquid-liquid extraction process whereby at least some interfering substances are preferentially retained in one liquid phase and the pesticide residues are retained in the other. For example, certain pigments, fats or waxes partition into the hexane solvent phase when swirled in contact with acetonitrile solvents, whereas chlorinated hydrocarbon pesticides are concentrated in the acetonitrile (Ref. 10). After separation of the immiscible phases, the pesticide residues are recovered by diluting the acetonitrile phase with water and back extracting with hexane. Concentrating the hexane phase to a small volume prepares the pesticide sample for either further cleanup or direct analytical determination. For detailed examples, see Reference 10.

4.2 Partition Chromatography

Partition chromatography is a form of liquid-liquid partition in which one of the immiscible liquid phases, for example, the polar (or water soluble) phase, is saturated onto a solid supporting phase such as silica gel, Florisil^R or alumina. This material is packed into a chromatographic column and the sample is eluted through this column with an immiscible non-polar solvent, e.g., hexane. See Reference 9 for examples.

4.3 Adsorption

Where interfering substances (e.g., some pigments and nonsaponifiable lipids) partition similarly to pesticide residues, other cleanup procedures may be required. Selective adsorption on an active solid (e.g., activated carbon, Florisil^R, activated alumina) can be employed to remove interferences (Ref. 10). Such material may be employed as a filter bed to selectively retain either the undesired interferences or the desired pesticide sample. Where pesticides and unwanted interferences have similar affinities for the adsorbent with solvents in general, a careful, graded separation may be necessary in which the adsorbent is placed in a cylindrical column (adsorption chromatography).

4.4 Adsorption Chromatography

Adsorption chromatography is widely used to clean up natural waters and bottom mud extracts (see Ref. 9). Adsorption chromatography can range from little more than a cylindrical filtration bed to crudely separate unwanted impurities to highly refined gradient solvent elution techniques, with various sample detectors, recorders and automatic sample collection devices. The sample sensitivity and resolution generally cannot compare with gas chromatography but separations can be made sufficiently definitive to effect significant pesticide sample cleanup. A number of examples are described by Van Middelem (Ref. 10) and other pertinent reviews are listed by Thornburg (Ref. 7). Florisil^R is a standard chromatographic adsorbent for chlorinated hydrocarbons (Ref. 1), while silica gel is prevalent in more general pesticide applications (Ref. 9). Chromatographic procedures are described in detail in References 1-5.

Thin-layer chromatography (TLC) is a special form of adsorption chromatography performed much like paper chromatography (see section 6). It is relatively simple, inexpensive and convenient and for a time seemed likely to supplant column adsorption chromatography for cleanup. However, because of greater pesticide sample losses with TLC, possibly owing to the large relative surface exposure to ambient oxygen and light, small scale column chromatography is currently receiving preference in cleanup operations (Ref. 1, 17). Even so, TLC still finds use as a final qualitative and semi-quantitative tool in some pesticide analyses, particularly metabolites.

4.5 Volatilization

Sweep co-distillation or forced draft volatilization are terms which have been given to techniques whereby pesticides are volatilized in a stream of inert gas and separated from non-volatiles. Volatized pesticides are collected at a cold trap. Basic description of this technique can be found under Storherr and Watts (Ref. 20), Watts and Storherr (Ref. 21), Gunther *et al.*(Ref. 22) and Mistres and Barthes (Ref. 23) as well as summaries in References 9 and 10. The technique is more applicable to tissue extracts than to the average aquatic sample.

5. Separation, Quantitation, and Tentative Identification of Organic Pesticide Residues

Several analytical techniques are available for the separation, tentative identification, and assay of organic pesticides from soil, water, food, animal and plant extracts. These usually are chromatographic techniques designed to separate various pesticide residues, and tentatively identify them prior to other methods of confirmation (Ref. 9). In 1971 Van Middelem (Ref. 10) stated:

> "Chromatography is the technique universally available and most used by the residue analyst for the qualitative separation of complex pesticidal mixtures and their quantitation. It is also a powerful aid in the identification of compounds.
>
> "In the past five years thin-layer and gas chromatography have become accepted widely in the residue field for segregation, identification, and measurement of mirco amounts of pesticides..."

In his 1973 review, "Pesticide Residues," Thornburg (Ref. 7) offers the following observations:

> "Publication in the field of pesticide methodology has continued at a

high level during the two-year review period from November 1970 through November 1972...

"This reivew period has been characterized by both improvements in existing techniques and the development of new instrumentation. Thin-layer chromatography is now a standard technique and an automatic instrument...has been developed, and research is being done on its application.

"Gas chromatography continues to be one of the most satisfactory procedures for the separation and quantitation of pesticide residues. These two years have seen continued improvement in techniques and equipment to allow more sensitive and accurate analysis of pesticide residues and pesticide metabolites....New high temperature packings have been made available and may prove satisfactory for hard-to-chromatograph pesticides.

"New detectors and new combinations of gas chromatography with other instruments promise much for the future. The most exciting prospects are likely to come from combinations with mass spectrometry with the help of the computer.

"Reliable automatic injection devices for gas chromatographs are now being produced. However, completely automatic extraction, extract purification, and quantitation instrumentation is still not a reality.

"Sampling, sample preparation, extraction, and cleanup of the extracts are a very important part of pesticide residue analysis. The use of solvents and reagents, especially prepared for pesticide residue analysis, is highly recommended. The quality of TLC plates is somewhat variable; therefore, TLC plates from more than one manufacturer should be evaluated for use in a residue analysis.

"A revival of interest in liquid chromatography has been spearheaded by improvements in column packing, use of high pressure, and new detection procedures. However, liquid chromatography has not yet found extensive use in pesticide analysis, and its widespread acceptance will probably await the development of more specific detectors."

5.1 Chromatographic Separation, Identification

The foregoing comments indicate the central role that chromatographic methods play in the analysis of pesticides. It must be understood, however, that chromatography itself is simply a means of separating substances, in this case organic compounds (pesticides). In general, chromatography consists of three essential steps:

a) sample introduction;

b) sample movement through a selectively interacting, immobile medium to separate sample components;

c) detection of separated sample components at completion.

Detection methods vary widely in both sensitivity and specificity. *The more sensitive and specific the sample component detection is, the more rigorous the analytical method becomes.* Generally pesticide residue chromatographic detection methods cannot be made totally specific because of the multiplicity of similar organic compounds which give a similar response under the same chromatographic circumstances. Additional analytical information of a less ambiguous nature is needed to confirm the tentative pesticide identification. Sometimes because of convenience or cost this entails simply more chromatography to check similarity of sample behavior vs. known pesticide residue standards. Verification of a pesticide residue identification by a second different chromatographic analysis is generally regarded as the minimum requirement to identify a pesticide residue (Ref. 9). Otherwise, the identification of a residue remains tentative, though perhaps strongly suggestive.

5.2 Spectroscopic Confirmation

Since it is desirable that the identification be unambiguous, spectroscopic analytical methods which provide spectra uniquely characteristic of specific organic compounds may be required. Initially, infrared absorption (IR) spectroscopy was utilized for this purpose in pesticide residue analysis; however, the quantities of residue available often were far below the minimum sampling requirements (e.g., 1 μg) for convenient routine operation. Mass spectrometry (MS), though more complex and expensive, has proven more successful because of its great sensitivity (0.1 μg to 0.1 ng) and molecular definition. MS can be employed in spectral analyses of individual chromatographic fractions to:

a) identify the pesticide residue isolated,

b) determine the purity of the pesticide residue isolated.

Mass spectrometers can also be designed or modified to accept GC effluent (separated components + carrier gas) for real-time GC-MS analysis. This is the most comprehensive, sensitive device presently available for pesticide residue analysis (see discussion in Section 9). Fourier transform real-time IR analysis of GC effluent is currently being investigated for applicability to pesticide residue analysis (Ref. 24).

6. Thin-Layer Chromatography (TLC)

TLC is a form of adsorption chromatography (see also section 4.4) adapted for organic microanalysis. TLC is performed much like paper chromatography and according to Van Middelem (Ref. 10), TLC is "more rapid, provides better resolution, and is more sensitive." TLC also requires less preanalysis sample cleanup.

6.1 TLC Operating Principle

In TLC, slightly volatile to nonvolatile organic compounds (e.g., pesticide residues) are dissolved in an organic solvent or solvent mixture which is caused to migrate along a thin layer of chromatographic adsorbent. The rate of migration of each specific pesticide residue depends on its comparative physicochemical affinity for the solvent (mobile) phase vs. the adsorbent (stationary) phase. The resolution or separation of similar compounds depends upon the chemical nature of the adsorbent, the thinness of the layer, the fineness of the adsorbent particles, and the choice of solvent(s).

TLC embodies the three chromatographic steps outlined in section 5.1. A minimum of equipment is required:

a) TLC plates, commercially available precoated with adsorbent surface, commonly 0.25 x 5 x 20 cm or 0.25 x 20 x 20 cm;

b) developing tanks to accept one or more TLC plates;

c) pesticide quality solvents;

d) color-developing (chromogenic) spray reagents and/or ultra-violet light source;

e) ventilated laboratory hood.

Chromatography takes place on glass plates coated with a thin layer (e.g., 0.25 mm) of polar adsorbent, usually partially hydrated silica gel ($SiO_2 \cdot XH_2O$) or alumina ($Al_2O_3 \cdot XH_2O$), bound to the glass with an inert adhesive (e.g., plaster of Paris: $CaSO_4 \cdot XH_2O$). A solution of the sample is spotted onto the adsorbent layer near one edge of the plate. The plate is then placed on end in an air tight container (developing tank) provided with a shallow pool of elution solvent a few mm below the sample spot. Capillary attraction causes the solvent in contact with the plate to rise upward along the plate, carrying sample components in that direction. The ratio of the distance the sample components travel compared to the distance of the solvent front (R_f) depends upon the chemical structure of the pesticide residues, and the nature of the solvent (mobile) phase and the adsorbent (stationary) phase as described above. Typical solvents require about 40 min to travel upward 15 cm which is a convenient point to terminate chromatography by simply removing the plate from the tank. Solvent generally evaporates within minutes. The chromatogram is then evaluated by spraying with a specific chromogenic (color developing) reagent. Laboratory practice for aquatic environmental pesticide residue analysis is discussed in References 3, 4 and 25.

6.2 TLC Analysis

In the analysis of pesticide residues associated with the aquatic environment, TLC can be employed to separate and tentatively identify individual pesticides, metabolites, transformation products, etc., subject to the limitations mentioned in section 4.4. The 1966 analytical methods manual (Ref. 3) of the Federal Water Pollution Control Administration (FWPCA) contains detailed information on specific TLC procedures for pesticide residue analysis. However by 1971 the methods manual (Ref. 4) of the FWPCA's successor, the EPA, provides only minimal TLC information, strongly suggesting that in accord with commentary in section 4.4, TLC now plays a lesser role in aquatic pesticide residue analysis. Significantly, the U.S. Geological Survey's manual (Ref. 5) omits all reference to TCL procedures for analysis of pesticide residues in water. Thus, although Van Middelem (Ref. 10) credited TLC with being a more useful method than paper chromatography and cites several examples of its use, *TLC appears to be limited to pesticides which are too labile for GC (e.g., metabolites) or to laboratories unable to afford GC.* Faust and Suffet (Ref. 9) did not find TLC applied extensively to aquatic extracts, but special cases are discussed. Table 2 summarizes conditions required for TLC separation for several types of organic pesticides.

TABLE 2.

General Conditions Required for Thin Layer Chromatographic Separation of Certain Organic Pesticides (from Ref. 9).

Pesticide Type	Absorbent	Solvent	Developer	Sensitivity
Chlorinated hydrocarbon	Silica gel G	CCl_4	$AgNO_3$-UV;Br_2-fluoroscein-$AgNO_3$	—
	Aluminum oxide G	*n*-Heptane, acetone	$AgNO_3$-2-PE	—
	Aluminum oxide G, Silica gel G	*n*-Heptane: acetone	$AgNO_3$-2-PE	0.01, 0.05, 0.1 μg
Phenoxy acid	Silica gel G and Kieselguhr G	Petroleum ether benzene, gl. acetic acid	$AgNO_3$-2-PE	—
Organic phosphate	Aluminum oxide G	15 and 20% DMF/ methyl cyclohexane	$AgNO_3$-citric acid-TBPP	0.05, 0.1 μg
	Alumina-neut., silica gel G	Benzene: acetone	BPB	0.1-0.2 μg
	Kieselguhr G	15% Acetone in hexane	Br_2-enzymes	5.0 ng
	Silica gel G	1,2-DCE: benzene	4-NP	2.0 μg
Diazinon, parathion	Silica gel G	Acetone	0.7% EtOH $CHCl_3$	—
Triazine	Silica gel G	$CHCl_3$ Acetone	Br_2-Brilliant green	—
Mixed pesticides	Silica gel G	CCl_4	$AgNO_3$-UV	—

7. Gas Chromatography

Within the past decade the gas chromatograph has become the dominant analytical tool in both quantitative estimation of pesticide residues and their tentative qualitative identification. This is due largely to the fact that (a) GC is capable of separating a considerable number of pesticide residues (or derivatives) in a short time without undue loss of sample components from decomposition, and (b) GC detectors combine high sensitivity (10 ng to 10 pg) with selectivity according to chemical features of the pesticide residue molecules (Table 3). For example, GC detectors are available that respond only to halogens (chlorine, bromine, and iodine). Owing to their general absence, bromine and iodine seldom interfere with chlorine detection, which makes such a detector very useful when analyzing for chlorinated hydrocarbon pesticide residues. Other detectors are specific for phosphorus, sulfur or nitrogen. Complete GC instrumentation suitable for aquatic pesticide residue analysis is generally available in the $4,000 - $9,000 price range.

7.1 GC Operating Principle

Analysis by GC embodies the three essential chromatographic steps mentioned in section 5.1. Basically gas chromatography functions by a partitioning effect on sample components (pesticide residues) between existence as a vapor in the mobile phase (carrier gas) and existence as a solute in a stationary (liquid) phase coated on an inert support material.

The pesticide residue sample is introduced in solution by injection with a miniature, needle-tipped syringe through a temperature-resistant silicon rubber septum (Figures 1, 4). Upon injection, the pesticide residue sample enters a glass lined chamber whose temperature can be adjusted for optimum sample vaporization. In the injection chamber the sample "plug" also encounters the flow of an inert carrier gas, usually either high purity nitrogen (N_2) or helium (He). The carrier gas transports pesticide residue components through a glass tube (GC column) containing a packing of an inert support material coated with a thin film of non-volatile liquid (stationary) phase in intimate contact with the mobile vapor phase (carrier gas + pesticide components). The vaporized organic pesticide components travel along the GC column according to their relative volatility and inversely according to their physicochemical affinity for the stationary liquid phase at the temperature of operation. The temperature, physicochemical nature and concentration of the liquid phase are selected for best resolution (separation) of the pesticide sample mixture into its constituents.

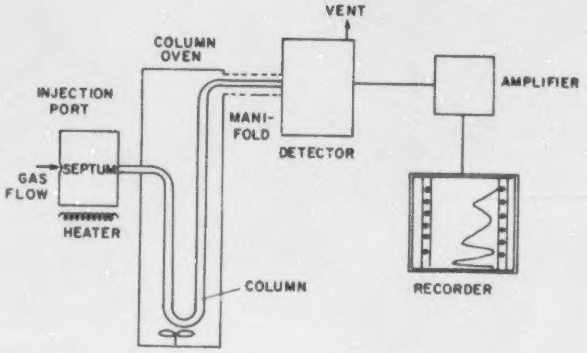


Figure 1. Schematic diagram of the gas chromatograph (from Ref. 26).

After a characteristic interval (retention time) the individual, separated pesticide residues (or derivatives) emerge from the GC column and are monitored by a sensing device (detector) that permits recording of their passage as a time-based analog signal rising above the detector background signal (baseline). Digitial recording and data handling of the detector signal is feasible and generally desirable where many samples must be analyzed.

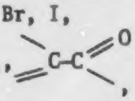
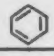
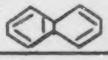
A large variety of permeable but low-volatility, polymeric organic liquids are commercially available as stationary phases for pesticide analysis (see catalogs, Ref. 27-29). Best operational performance is secured from GC liquids which have a high thermal stability. It is important that the liquid-phase decomposition products (column bleed) not interfere with detector operations.

The liquid phase should present a sufficiently thin surface film to the sample components to allow virtually instantaneous equilibration between the liquid and vapor phases. At the same time there should be sufficient liquid phase present to avoid its being swamped by normal quantities of sample components such that these solutes predominate to act as solvent and "wash down" or strip the GC column. To accomplish these objectives, a high surface-to-volume (or mass) ratio is achieved in the support material by using highly porous diatomite granules. When size-graded, deactivated (acid-washed, silanized) solid support material is coated uniformly with a few percent of the GC liquid phase(s) of choice, it is suitable for GC column packing.

Packed GC columns made from Pyrex tubing (for inertness) are employed almost universally in pesticide residue GC analysis. Usually the glass tubing is inserted into the injection chamber close to the septum so that once the residue sample has been injected by the syringe, the sample components do not contact hot metal surfaces until they have passed through the column and enter the

TABLE 3.

Detectors for GC Analysis of Pesticide Residues

Detector*	Chemical Functionality	Pesticide Sensitivity (g)	Linear Range
ECD (many variations)	Cl, Br, I, $-NO_2$,  , , etc.	10^{-11}	10^2 to 10^4
MCD-1	Cl, Br, I	10^{-9}	10^3
MCD-2	S	10^{-8}	10^3
MCD-3	N	10^{-8}	10^3
CCD-1	N	10^{-9}	10^3
CCD-2	Cl, Br, I	10^{-9}	10^3
CCD-3	S	10^{-9}	10^3
TID-1	P	10^{-11}	10^3
TID-2	N, P (S, I)	10^{-10}	10^4
FPD-1	S	10^{-9}	10^3 (log)
FPD-2	P	10^{-10}	10^4

* Detector types abbreviated as follows:

ECD = Electron Capture Detector
MCD = Microcoulometric Detector
CCD = Coulson conductimetric Detector
TID = Thermionic (alkali-flame) Detector
FPD = Flame Photometric Detector

detector. This feature, called "on-column injection", is particularly important in pesticide analysis because of possible instability of these molecules in contact with hot metal (e.g., stainless steel) surfaces.

Similarly, the column packing must be inert toward pesticides. The most commonly employed support material is a so-called flux-calcined diatomaceous earth which has been deactivated by acid-washing and silanization (surface reaction with silicone blocking groups). It is commercially available under several trade names: Chromosorb W-HP, Anakrom ABS, Gas-Chrom Q, among the more common (Ref. 27-29).

A GC column widely used for pesticide residue analysis is the upright Pyrex U-tube in 1- to 2-meter overall lengths and 2-mm inside diameter (I.D.). In this configuration a special, close-tolerance 6.2-mm outside diameter (O.D.) Pyrex tubing (nominally 1/4" O.D.) is often used. Other I.D.s (3, 4 mm) are also available. Coiled 1/8" and 1/4" O.D. Pyrex GC columns must be used with many GC instruments, but are not preferred over the upright U-tubes which are easier to pack. U-tubes require larger and taller GC column ovens, commonly referred to as "biomedical" type; whereas, coiled Pyrex columns are employed in ovens designed primarily for metal columns. Glass capillary GC columns are not commercially available in the U.S. Metal columns, including capillaries, are not generally recommended for pesticide residue analysis because of their potential reactivity toward sample molecules.

Flexible, precise control of the GC column oven temperature is essential to assure uniform reproducible operating conditions and to prevent overheating of the liquid partitioning phase. Most commercial GC instruments not only provide for rapid temperature stabilization (± 1°C) but also can be adapted to increase the temperature at various selectable rates during the chromatographic run (chromatogram). This feature, known as temperature programming, can be useful in accelerating the analyses of pesticide residues which are widely separated in their GC retention times. This allows prompt analysis of rather involatile residues in the presence of the more volatile residues.

7.2 GC Detectors for Pesticide Residues

The trace levels of pesticide residues in samples related to the aquatic environment (as low as 1 ng/l) require GC detectors that are both highly sensitive and selective. Hence, two common GC detectors are not particularly useful: the ordinary flame ionization detector (FID) and the thermal conductivity detector (TCD). However, a number of other detection devices are useful, depending on the degree of sensitivity and selectivity desired (see Table 3 and discussion below). Faust and Suffet (Ref. 9) have pointed out that no conventional detector can entirely overcome interferences from molecules having chemical features similar to pesticide molecules, nor can sample cleanup procedures designed to exclude such interferences be assumed to be complete. Van Middelem (Ref. 10) estimated that there is at least a tenfold decrease in sensitivity for pesticide residues obtained from biological matrices as compared to pure reference compounds in pure solvents. For such samples the sensitivities listed in Table 3 would be poorer.

GC detectors suitable for pesticide residue analysis have been discussed in terms of *specificity* and *nonspecificity* (Ref. 9, 29), although *degree of selectivity* may be more accurate. For example, a high degree of pesticide residue detection selectivity may be obtained from a sophisticated GC detector--the specific-ion detecting mass spectrometer (discussed in Section 9). Almost complete specificity can be obtained from this combination of GC and MS data (known as specific-ion chromatography), although the apparatus costs many times more than conventional GC instruments. Westlake and Gunther (Ref. 30) have reviewed the role of various conventional GC detectors for pesticide analysis, some details of which are included below.

7.2.1 Electron Capture Detector (ECD).

The most widely used detector for general pesticide residue analysis unquestionably is that based on electron capture. With the ECD a steady current of high-energy electrons (beta rays) emanates from a radioactive source such as tritium (H^3) or nickel-63 (Ni^{63}). As the carrier gas (e.g., nitrogen) bearing the separated GC sample components flows through the detector cell (Fig. 2), the beta rays from the source ionize the carrier gas, forming slow (thermal) electrons which can be collected as a measurable standing current at the anode. When separated GC sample components capable of capturing slow electrons pass through the cell, the standing current is reduced. This reduction is measured by a sensitive amplifier system and converted into a signal suitable for millivolt strip-chart recorders (Fig. 3).

Depending on the geometry of the electron capture cell and other factors, pulsed d.c. operation of the polarizing voltage may provide best sensitivity. A pulse of a few μsec duration at intervals of 10 to 100 times the pulse width can remove high-energy electrons while generating the necessary thermal electrons more susceptible to capture by GC effluent components.

ECD responds to a number of chemical functionalities (Table 3) having varying degrees of electron affinity, but it is employed primarily to screen for chlorinated pesticide residues, detecting nanogram to picogram quantities (see Figure 3). Solvents must be checked for interferences, and redistilled if necessary. Environmental

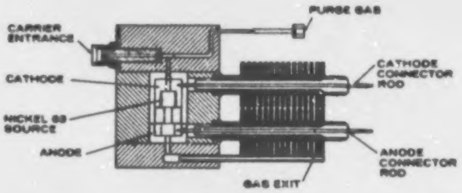
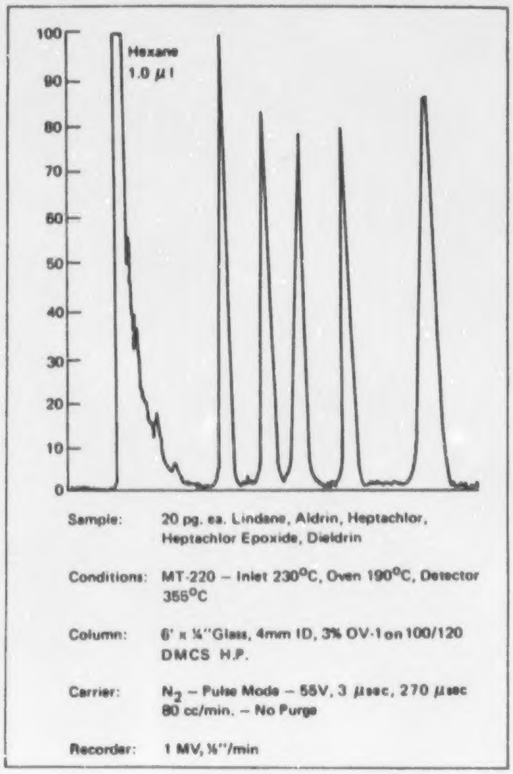

PURGE GAS
CARRIER ENTRANCE
CATHODE
NICKEL 63 SOURCE
ANODE
CATHODE CONNECTOR ROD
ANODE CONNECTOR ROD
GAS EXIT

FIGURE 2. *High temperature ECD with Ni^{63} source and concentric geometry (from Ref. 31).*



Sample: 20 pg. ea. Lindane, Aldrin, Heptachlor, Heptachlor Epoxide, Dieldrin

Conditions: MT-220 – Inlet 230°C, Oven 190°C, Detector 355°C

Column: 6' x ¼"Glass, 4mm ID, 3% OV-1 on 100/120 DMCS H.P.

Carrier: N_2 – Pulse Mode – 55V, 3 µsec, 270 µsec 80 cc/min. – No Purge

Recorder: 1 MV, ½"/min

FIGURE 3. *GC analysis of chlorinated hydrocarbons using the ECD of Figure 2 (from Ref. 31).*

samples generally require preanalysis cleanup. The polychlorinated biphenyls (PCBs) give numerous GC peaks which interfere with chlorinated hydrocarbon analysis and present serious cleanup problems. On the other hand the many PCBs manifest an environmental insult comparable to the chlorinated hydrocarbon pesticides, so their detection by ECD can be made an advantage.

ECD has been applied to GC analysis of all categories of pesticide residues (Ref. 10); chlorinated hydrocarbon insecticide analysis predominates followed by the organophosphate insecticide parathion. ECD-GC also applies to chlorinated phenoxyalkanoic acid herbicides after they have been esterified (Ref. 5).

Several sources of beta radiation are commercially available under licensing by the Atomic Energy Commission. Titanium tritide (TiH^3) beta sources are less expensive than Ni^{63} but they are chemically stable only up to 220°C detector temperature (H_2^3 evolution!). This temperature is somewhat low to prevent sample or column decomposition products from condensing on the emitting surface and reducing the ECD sensitivity. The more expensive Ni^{63} sources (2-15 millicuries) are safe up to 400°C which retards condensation and permits bake-out. Return to manufacturer is advised for cleaning. In general Ni^{63} sources have been preferred for pesticide residue analysis.

Scandium tritide sources have been described (Ref. 32) which retain the superior source characteristics of tritium while attaining a desirable temperature stability (> 325°C).

If chlorinated solvents such as methylene chloride, chloroform and carbon tetrachloride are employed anywhere in the sample preparation steps, care must be taken to insure their virtual complete evaporation, since microgram quantities can render an ECD temporarily inoperative. Further operational details may be found in References 2-5, 10, 25, 29 and references cited therin and manufacturers' bulletins.

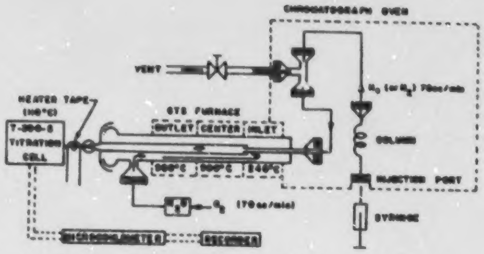
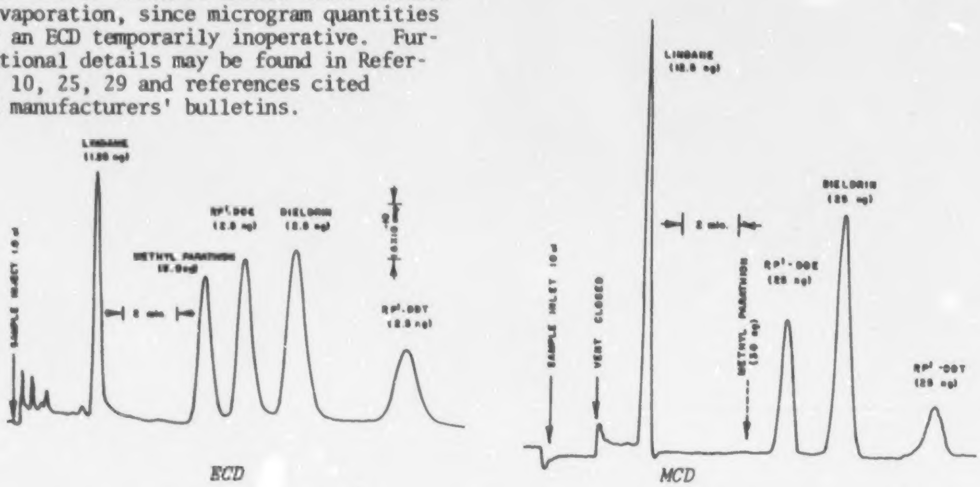


FIGURE 4. *Schematic of MCD-GC (from Ref. 34).*

7.2.2 Microcoulometric Detector (MCD).

Around 1960 Coulson and associates developed the first detector specifically designed for pesticide residue analysis (Ref. 9). The first application was specific for chlorine, bromine and iodine. Later modifications adapted it for sulfur (Ref. 33) and nitrogen (Ref. 34) detection.

In the most recent version (Ref. 35), GC effluent (carrier gas + sample components) is passed through a combustion tube (Fig. 4) where the organics are catalytically oxidized with humidified O_2 to H_2O, CO_2. If chlorine or sulfur are present, HCl or SO_2 are also formed. To detect halogenated (e.g., chlorinated) pesticides specifically, the combustion products are passed directly to the silver (Ag) sensing electrode in a titration cell. Any HCl present is converted to silver chloride (AgCl), creating an electrical imbalance in the cell. The current required to regenerate Ag from AgCl is measured on a recorder and the time integral of the current curve indicates the amount of Cl present.



ECD MCD

FIGURE 5. *GC analysis of pesticides comparing the sensitivity and selectivity of a 5-millicurie ECD vs. a halogen-detecting MCD (from Ref. 34).*

Sulfur is determined by a different cell in which SO_2 is oxidized to sulfate by iodine (Ref. 33). Again electrical imbalance is detected and restored by regenerating the iodine to its original level. The measured current indicates the amount of sulfur present as SO_2.

Since bromine- or iodine-containing organics are seldom encountered in residue analyses, the MCD is virtually exclusively a Cl detector. In one exception, the herbicide, bromacil, has been determined by MCD-GC (Ref. 36). Although the MCD is more selective than the ECD, it is about 100 times less sensitive (Table 3).

7.2.3 Coulson Conductivity Detector (CCD).

Coulson has also utilized electrolytic conductivity for detecting nitrogenous organic compounds, e.g., carbamates (Ref. 37). Reductive combustion of nitrogenous GC effluent components in a hydrogen atmosphere over a nickel catalyst at 900°C (Figure 6) produces ammonia which is trapped in a stream of deionized water flowing through a conductivity cell. H_2S, HCl and other volatile acids are removed in passage through $BaCO_3$ or $Sr(OH)_2$ absorbent filters (Ref. 38) and thus do not interfere. Nanogram nitrogen sensitivity is customary with no detectable interference from nitrogen-free compounds. This may minimize the necessity for preanalysis cleanup (Fig. 7).

Reductive combustion of pesticide residues under hydrogen without a catalyst or an absorbent filter allows detection of halogens as acids (HCl, HBr, HI) without significant interferences. When oxidative combustion over platinum catalyst at 900°C is employed, halogen (Cl, Br, I) and sulfur-containing pesticides may be determined. The CCD becomes specific for either halogen or sulfur through the use of selective absorbents (Ref. 39). Sensitivity for chlorinated hydrocarbons compares favorably with that of the MCD (Table 8) and the response is faster (Fig. 8).

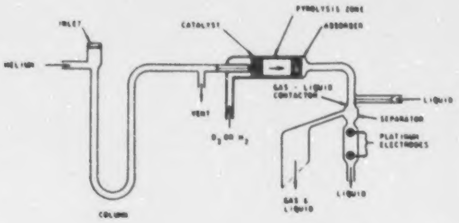


FIGURE 6. Schematic of the CCD (from Ref. 39)

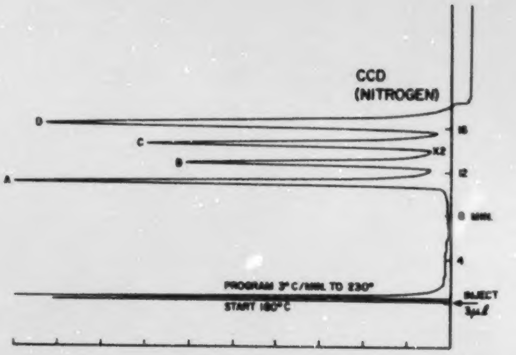


FIGURE 7. CCD analysis of triazine pesticides. A: prometone (200 ng), B: propazine (100 ng), C: atrazine (25 ng), D: simazine (50 ng). Column: 1/4-in. x 2-1/2-ft carbowax on chromosorb-HP. Column temperature: 180°-230°C at 3°C min. Carrier gas: helium, 80 ml/min (from Ref. 39).

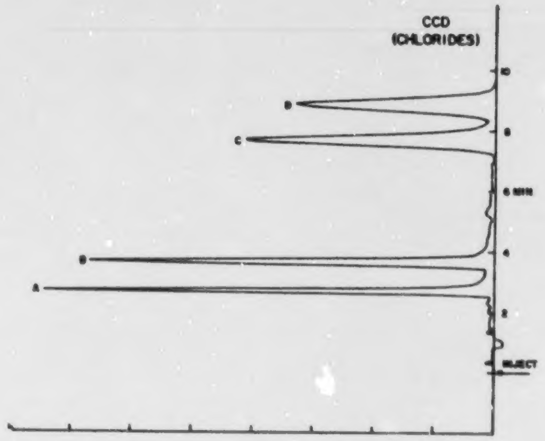


FIGURE 8. CCD analysis of chlorinated pesticides. A: lindane (30 ng), B: heptachlor (30 ng), C: dieldrin (50 ng), D: endrin (50 ng). Column: 1/4-in. x 6-ft glass, OV-1 on chromosorb-HP. Column temperature: 225°C. Carrier: helium, 80 ml/min. (from Ref. 39)

7.2.4 Thermionic Detector (TID)

Karmen and Giuffrida (Ref. 40) modified a flame ionization detector (FID) to attain a significant relative response to phosphorus. Improvements by Hartmann (Ref. 41) have led to the development of a thermionic detector highly specific for phosphorus. Physically this detector is much like a conventional FID except that the burner tip consists of a ceramic-like material containing cesium bromide. Compounds containing carbon or chlorine do not interfere when the hydrogen flow rate to the burner is very carefully controlled (e.g., 16.00 ± 0.01 ml/min). Dynamic range is about three orders of magnitude with sensitivity to 12 pg for parathion. In a similar burner (Fig. 9) using a different alkali salt (RuBr) an enhanced response was found for nitrogen-containing organics (Ref. 42). It is more sensitive than the CCD but less selective. Table 4 indicates some approximate comparisons. In general thermionic detectors are extremely sensitive to minor ambient pressure changes such as that from a door being opened or closed (Ref. 17).

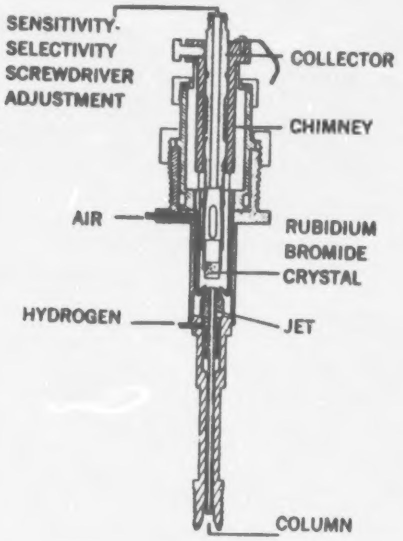


Figure 9. TID for nitrogen (from Ref. 42).

TABLE 4.

Approximate Comparative Selectivity of TID for Nitrogen (Fig. 10; from Ref. 42).

N : CH (Octadecane)	5000:1
N : Cl (1-Chlorooctadecane)	5000:1
N : Br (1-Bromododecane)	500:1
N : S (Thioanisole)	200:1
N : I (*p*-Iodotoluene)	100:1
N : P (Parathion)	1:10

7.2.5 Flame Photometric Detector (FPD)

Brody and Chaney (Ref. 43) modified an FID to make a photometric detector for determining pesticides containing sulfur (S) or phosphorus (P). Chemiluminescence (light emission) results when these elements in GC effluent components are mixed with air and oxygen and burned in a hydrogen atmosphere. This permits S or P detection by using interference filters in conjunction with a photomultiplier (Fig. 10). At the same time the FPD can also be operated as an FID but generally at only a fraction of the usual FID sensitivity.

The interference filters are chosen for maximum rejection of light not at the wavelength of interest. For phosphorus it is 526 nm, corresponding to chemiluminescence of the HPO species in the hydrogen rich flame. For sulfur, 394 nm is suitable to detect the S_2 species. A twin P, S detector is also available to allow simultaneous, independent P and S detection as shown in the chromatogram of Figure 11.

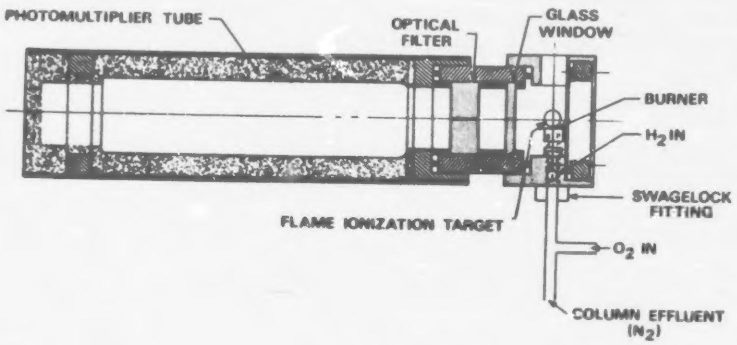


Figure 10. FPD schematic (from Ref. 37).

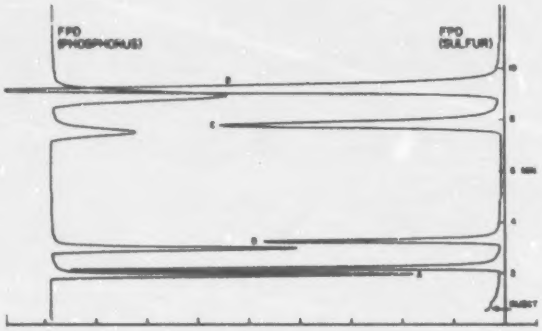


Figure 11. Dual FPD analysis of thiophosphate pesticides A: methyl parathion, B: parathion, C: methyl trithion, D: ethion. Sample: 5 µl (1 ng/µl). Column: 1/4-in. x 6-ft glass, OV-1 on chromosorb-HP. Column temperature: 200°C. Carrier gas: nitrogen, 80 ml/min (from Ref. 37).

7.3 GC Analysis

Gas chromatographic procedures for analysis of pesticide residues found in aquatic environments are given in References 1-5. Since these publications contain standard analytical procedures developed under official or quasi-official sponsorship, a chronological comparison of their differences reveals some of the trends in pesticide residue analysis during the past decade. For example, in 1966 a single GC column was recommended (Ref. 3). Subsequently, at least two GC columns were recommended (Ref. 2, 4, 5) and in the EPA manual (Ref. 4) four standard GC columns were described. Improvements in GC practice are evident in the recent publications (Ref. 4,5; see Table 5), viz. (a) the sole use of pyrex glass columns, (b) more inert diatomite support, (Gas Chrom Q: acid-washed, silanized), which in turn permits (c) lighter liquid phase loadings (%). Trends to smaller bore (I.D.) columns (< 2 mm vs. > 4 mm) and more narrowly graded mesh (80/90 or 80/100 vs. 60/80) which improve chromatographic resolution are also apparent. Reference 4 describes the use of recently introduced liquid phases having improved thermal stability.

TABLE 5.

Comparison of Official Standard GC Methods of Analysis for Aquatic Pesticide Residues

Ref.	Column			Packing			Coating
	Material	Length (feet)	I.D. (mm)	Mesh	Support (diatomite)	Treatment*	
3	Pyrex or Aluminum	4	≥ 4	60/80	Chromosorb P	A	5% DC-200
2	(1) Pyrex	6	2-4	80/90	Anakrom	ABS(F)	10% DC-200
	(2) "	"	"	"	"	"	4% DC-200 + 6% QF-1
4	(1) "	"	"	80/100	Gas Chrom Q	AS(F)	3% DC-200 + 5% QF-1
	(2) "	"	"	"	"	"	3% OV-101
	(3) "	"	"	60/80	"	"	5% OV-17
	(4) "	"	"	80/100	"	"	3% OV-210
5	(1) "	"	≤ 2	60/80	"	"	5% DC-200 + 0.5% Carbowax 20M
	(2) "	"	"	"	"	"	5% QF-1 + 0.5% Carbowax 20M

*A: *Acid-washed*
B: *Base-washed* (F): *Flux-calcined*
S: *Silanized*

Although the old Federal Water Pollution Control manual (Ref. 3) lists only a single standard GC column, it does recommend screening GC samples with an ECD which is highly sensitive to chlorinated hydrocarbons and parathion (ca. 10^{-11}g), and then confirming their presence by MCD-GC. Of course, parathion shows no peak by MCD (see Fig. 5), a fact which can be used to confirm its probable presence by ECD. The 13th edition of "Standard Methods" (Ref. 2) does list two satisfactory GC procedures, an improvement over (Ref. 3) but it *fails* to make use of the more specific GC detectors (MCD, CCD, FPD, TID) for confirming the pesticide residue identification. *Thus a major reference on water analysis (Ref. 2) relies only on a second GC analysis to confirm the pesticide residues present.* The EPA manual (Ref. 4) states:

> "Reasonably positive identification of a pesticide is obtained by corroborating results, using at least two different types of gas chromatographic columns."

But it also states:

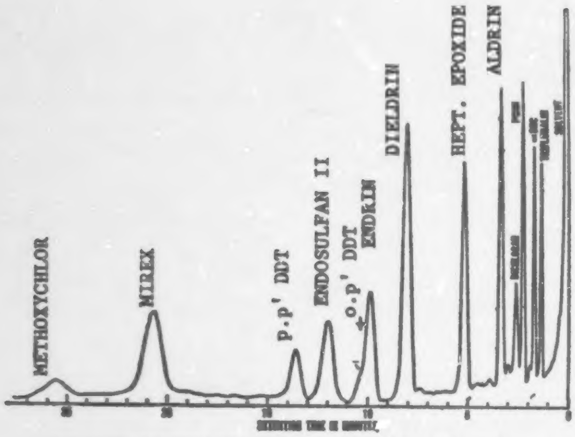
> "The qualitative identification of a pesticide should be confirmed using infrared spectroscopy or mass spectroscopy whenever instrumentation is available and/or the quantity of the compound permits. If this is not possible, gas chromatographic analysis using additional unlike columns and other selective detectors is recommended."

For this purpose the EPA manual (Ref. 4) describes four recommended GC columns (see Table 5) and four GC detectors (those in Sections 7.2.1 - 7.2.3, 7.2.5). The U.S. Geological Survey manual (Ref. 5) lists two recommended GC columns and three GC detectors (those in Sections 7.2.1 - 7.2.3). The most recent recommendations (App. 2) have been entered into the Federal Register (Ref. 1). Gas chromatograms are shown in Figure 12. Also listed are the very important relative retention times (RRt) on these GC columns (Table 6) for 19 resolved compounds (Aldrin RRT = 1.00).

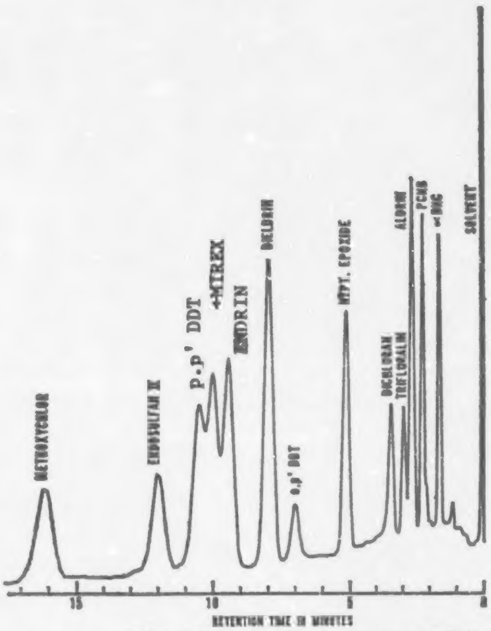
Table 6 — Retention ratios of various organochlorine pesticides to aldrin (from Ref. 1).

Liquid Phase[1]	1.5% OV-17 + 2.95% QF-1	5% OV-210	3% OV-1	6% QF-1 + 4% SE-30
Column Temp	200 C	180 C	180 C	200 C
Argon/Methane Carrier Flow	60 ml/min	70 ml/min	70 ml/min	60 ml/min
Pesticide	RRt	RRt	RRt	RRt
Trifluralin	0.39	1.11	0.33	0.57
α-BHC	0.54	0.64	0.35	0.49
PCNB	0.68	0.85	0.49	0.63
Lindane	0.69	0.81	0.44	0.60
Dichloran	0.77	1.29	0.49	0.70
Heptachlor	0.82	0.87	0.78	0.83
Aldrin	1.00	1.00	1.00	1.00
Heptachlor Epoxide	1.54	1.93	1.28	1.43
Thiodan I	1.95	2.48	1.62	1.79
p,p′-DDE	2.23	2.10	2.00	1.82
Dieldrin	2.40	3.00	1.93	2.12
Captan	2.59	4.09	1.22	1.94
Endrin	2.93	3.56	2.18	2.42
o,p′-DDT	3.16	2.70	2.69	2.39
p,p′-DDD	3.48	3.75	2.61	2.55
Thiodan II	3.59	4.59	2.25	2.72
p,p′-DDT	4.18	4.07	3.50	3.12
Mirex	6.1	3.78	6.6	4.79
Methoxychlor	7.6	6.5	5.7	4.60
Aldrin (Min. absolute)	3.5	2.6	4.0	5.6

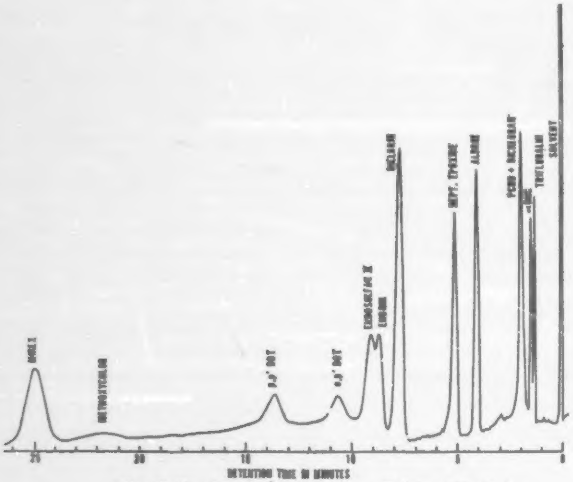
[1] All columns glass, 180 cm x 4 mm ID, solid support Gas-Chrom Q (100/120 mesh).



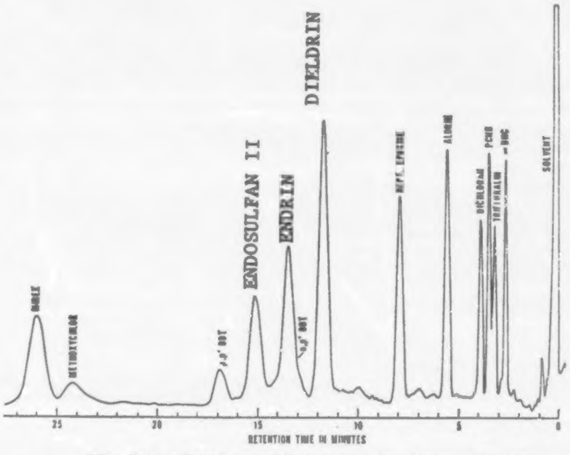
Column Packing: 1.5% OV-17 + 1.95% QF-1, Carrier Gas: Argon/Methane at 60 ml/min, Column Temperature: 200 C, Detector: Electron Capture.



Column Packing: 5% OV-210, Carrier Gas: Argon/Methane at 70 ml/min, Column Temperature: 180 C, Detector: Electron Capture.



Column Packing: 3% OV-1, Carrier Gas: Argon/Methane at 70 ml/min, Column Temperature: 180 C, Detector: Electron Capture.



Column Packing: 6% QF-1 + 4% SE-30, Carrier Gas: Argon/Methane at 60 ml/min, Column Temperature: 200 C, Detector: Electron Capture.

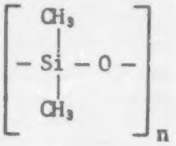
Figure 12. Electron capture gas chromatograms of pesticide standards (from Ref. 1).

7.4 GC Liquid Phases

The recommended liquid phases (Ref. 2-5) fall into three main categories: silicones, fluorocarbons and polyethers.

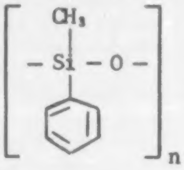
7.4.1 Silicones

Several types of silicone polymers are employed as partitioning GC liquid phases. The most common is the poly dimethyl siloxane:



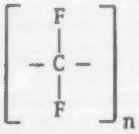
$$\left[-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O-\right]_n$$

This is the basic structure of DC-200 and OV-101 and many others including the so-called silicone gum rubbers such as SE-30 and OV-1. Another popular GC silicone is OV-17:



7.4.2 Fluorocarbons

Related to the familiar Teflon, fluorocarbon polymers for GC, e.g., QF-1, have the basic repeating structure:



$$\left[-\overset{\displaystyle F}{\underset{\displaystyle F}{C}}-\right]_n$$

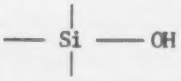
7.4.3 Polyethers

For pesticide GC work, polyethers are utilized mainly as liquid phase modifiers, such as reducing adsorptive effects (tailing) on GC peaks. Carbowax 20M, one of the best known, has the repeating structure:

$$\left[-CH_2-CH_2-O-\right]_n$$

7.4.4 Liquid Phase Support Material

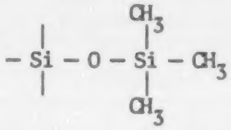
Currently the predominant choice of the granular support material on which the liquid phase is coated is a flux-calcined diatomaceous earth particle (see Table 5) which is relatively free of reactive effects while retaining a high surface area to volume ratio. Unlike the sturdy, pink precursor material (firebrick, Chromosorb P, etc.) this modified diatomite is white and rather fragile (crushable between fingers), so it should be handled with care. This is particularly true after it has been further treated by acid-washing (to remove traces of catalytic metal salts) and silanization: to convert surface



$$-\overset{|}{\underset{|}{Si}}-OH$$

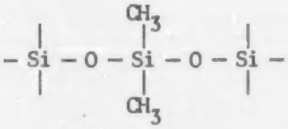
groups

to



$$-\overset{|}{\underset{|}{Si}}-O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-CH_3$$

or



$$-\overset{|}{\underset{|}{Si}}-O-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-O-\overset{|}{\underset{|}{Si}}-$$

Once the modified diatomite surface has been so treated, any breaking of the particle would result in a raw surface being exposed to the pesticide components.

7.5 Miscellaneous GC Applications to the Aquatic Environment

Most GC applications to aqueous extracts have been concerned with separation and identification of parent pesticides. Less attention has been directed to hydrolytic and metabolic products. Most efforts have been applied to chlorinated hydrocarbons. Information gathered from various aquatic studies follows:

Chlorinated hydrocarbon pesticides and/or their metabolites are resolved on both nonpolar liquid phases (e.g., DC-200, OV-101, SE-30, OV-17) and polar phases (e.g., QF-1, or OV-210) at sensitivities around 10 to 100 ng/l with ECD. Conditions used to analyze chlorinated hydrocarbons extracted from water and bottom muds have been summarized by Faust and Suffet (Ref. 9). Nonpolar or polar liquid phases are also used to separate the relatively polar organophosphates and their metabolites. Phases such as DC-200, SE-30, Carbowax 20M, and Reoplex-400 have been utilized effectively (Ref. 9).

A few techniques exist for GC separation of the phenoxyalkanoic acids and their esters in extracts of natural waters and bottom muds. Butenmann and Lisk (Ref. 44) report resolution of 2(2,4,5-TP) from interferences on a Dow silicone column with ECD (sensitivity: 0.05 mg/l). Goerlitz and LaMar (Ref. 45) provide MCD-GC data on 2,4-D, 2,4,5-T, and 2(2,4,5-TP) in aqueous extracts. These herbicides were extracted from acidified water in free acid form and methylated. They were then separated on a QF-1 column (sensitivity: 10 ng/l).

7.6 Limitations of GC

GC alone is insufficient for the positive, absolute identification of pesticides, metabolites, or hydrolysis products; hence, further analytical confirmation is needed. Indeed, a single, universally applicable system for isolation and separation of parent compounds, metabolites, and hydrolysis products may not always be possible. Sample aliquots at the minimum detectable limit for a particular pesticide may not be free of interferences in the chromatogram. Benyon and Elgar (Ref. 46) and Robinson and Richardson (Ref. 47) agree that one should not assume the presence of a particular pesticide on the basis of the gas chromatographic retention time determined with only one stationary phase. Natural compounds may be confused with pesticides by certain GC detectors. Often they are not completely removed by the cleanup procedures.

7.7 GC Summary

GC is a powerful analytical tool for separating and detecting aquatic pesticide trace residues (submicrograms). A multicolumn and detector approach is advised since no single GC system can separate and detect all organic pesticides. Confirmation of GC peaks from complementary procedures such as thin-layer or paper chromatography, IR or mass spectroscopy is important, particularly when the sample comes from a polluted aqueous environment.

8. Advanced Techniques

Although pesticide residue analysis has acquired a semblance of standardization within the past few years, the 1970's have seen a continued evolution of approaches. The situation has, in fact, changed sufficiently rapidly that badly needed reviews and books (e.g., Ref. 9, 10) have scarcely been able to stay abreast of current developments or foresee the future. One example is the evolution and proliferation of official GC methods discussed in Section 7.3. Subsequent GC developments have tended in the direction of on-line mass spectrometric detection (GC-MS) with computer data handling, in spite of the cost and sophistication of such instrumentation. During this time, reliance on TLC for pesticide residue separation and tentative identification, for sample cleanup, has declined in some laboratories (Ref. 17; see section 4.4), despite its relatively low cost. Continued R & D on TLC applications to residue analysis could, of course, reverse this trend. In this regard, an automatic, multiple-sample processing TLC instrument called "Chromatape" has been introduced by J.T. Baker Chemical Company (Ref. 49) which should improve separational consistency and quantitative precision. The cost is many times that of conventional TLC equipment. Thornburg (Ref. 7, 1973) reports a renewed interest in high pressure liquid chromatography (a mechanized form of partition chromatography, Section 4.2). However, widespread acceptance will probably require detectors better in both specificity and sensitivity.

What constitutes a satisfactory confirmation of a pesticide residue (i.e., verification of its identity) has been a continuing point of concern, especially for law enforcement situations. At first, analysts were fortunate to have a single method sufficiently sensitive and selective for the separation and tentative identification of residues in the same analytical step. In time, demands for greater laboratory convenience and analytical rigor led to more and better procedures. Nevertheless, definitive spectroscopic confirmation of chromatographic fractions (chromatographically separated sample components) has always been regarded as essential for unambiguous confirmation of residue identity. Certainly this is superior to the bare minimum of TLC confirmation of GC tentative identification or vice versa. From the first, infrared (IR) spectroscopy provided reasonably definitive characterization of organic pesticides and it was readily available as one of the more convenient analytical tools for identifying organic compounds. However, IR lacked satisfactory sensitivity, which made its application to pesticide residue identification cumbersome. Even with special accessories (microcells, beam condensers, signal averagers) to conventional instruments, μg IR sample sensitivity requires painstaking effort. As has been seen in Part A, ng/l or ng/kg are commonly encountered as pesticide residue levels in the environment. To close this sensitivity gap, a new technique, Fourier-Transform IR spectrometry with computer data handling (Ref. 50), is being investigated for suitability to operate on-line with GC to confirm the identity of separated pesticide residues (Ref. 51). Since the cost of such a system is comparable to that of a GC-MS system with computer data handling, it remains to be seen what advantages there may be.

9. Combined Gas Chromatography-Mass Spectrometry (GC-MS)

Regarding GC analysis of pesticide residues, Thornburg (Ref. 7, 1973) states: "The most exciting prospects are likely to come from combinations with mass spectrometry with the help of the computer." This has certainly been true for pesticide residue analysis within the EPA. After initially evaluating a single computerized, rapid-scanning mass spectrometer interfaced to a gas chromatograph, more than a dozen such units have been installed throughout the EPA. Most are located in the regional technical support laboratories. They are employed for analysis related to organic chemical pollutants such as pesticide residues, PCBs, petrochemicals, and other toxic or noxious organic contaminants.

9.1 MS Operating Principle

Organic mass spectrometry involves the ionization of organic molecules in high vacuum, generally by bombardment with 70 eV electrons. These organic ions are then accelerated, deflected and focussed by electrical and/or magnetic fields such that inertial (mass) differences allow the ions to be dispersed and displayed according to their respective mass/charge ratio (m/e). Since singly charged ions predominate, the deflection is a simple function of the mass for most ions. With electron ionization (EI) at 70 eV, organic molecules receive more than sufficient energy to dislodge an orbital electron and generate positively charged molecular ions. Excess energy imparted to the molecular ion may be released by various mechanisms involving rupture of the parent ion into neutral and ionic fragments. These, plus the parent molecular ion, constitute the principal features of the mass spectrum which is simply a statistical record of the abundance of ions at their respective m/e positions throughout the mass range scanned. On low resolution instruments, the molecular weight of an organic molecule and its characteristic fragmentation products, i.e., the mass spectrum is expressed in nominal atomic mass units (amu). This type of mass spectrometry affords the highest sensitivity, extending to 10^{-11} g.

An ionized molecule or fragment generally decomposes according to its intrinsic structural features, giving a characteristic reproducible pattern to the spectrum. In turn the structural fragmentation pattern can be used to reconstruct the original molecule. Generally, the highest mass cluster in the spectrum is due to singly charged molecular ions. Within this cluster, the heaviest masses, i.e., the highest mass lines, are due to the presence of one or more heavy atomic isotopes in some of the molecules. Sometimes fragmentation is so predominant that the molecular ion cannot be determined directly but must be inferred from the structural fragments observed. In such cases electron bombardment may be substituted by alternative ionizing processes which minimize fragmentation such as field ionization (FI), field desorption ionization, or chemical ionization (CI). For general pesticide analysis, however, it is not critical to observe the parent (molecular) ion if the fragmentation pattern is sufficiently definitive to identify the molecule unambiguously. The vast majority of the 10,000 mass spectra on file (Ref. 52) have been taken under EI conditions at ca. 70 eV where minor variations in ionizing voltage have little effect on the spectrum. Thus, standard EI spectra afford the widest possibility of confirming the identity of a pesticide residue. At the very least the identity can be narrowed to a small handful of compounds from among tens of thousands. The need for an alternative to EI has not yet been demonstrated for pesticide residue analysis. If such a need arises, CI is presently the most likely candidate to be employed with GC-MS instruments.

9.2 Basic MS Instrumentation

Several kinds of mass spectrometers are suitable for use with a gas chromatograph. Basically, all must have a source for generating the organic ions under vacuum, an analyzer for separating the ionic particles according to m/e, and an electron multiplier for detecting the ions (see Fig. 13-15). Other features such as GC interfacing, auxiliary sample inlets, vacuum systems, and spectrum recorders are also required. There is some variation in design and performance of the various components from manufacturer to manufacturer, hence MS instrumentation should be examined independently and in far greater detail than is possible herein. This survey will attempt to set forth some of the salient features relevant to GC-MS analysis of pesticide residues. The discussion will be limited to mass spectrometers which have been designed primarily for operation with GC effluent for which proven complete data systems are commercially available. Scanning speed, sensitivity, resolution and mass range are important parameters for comparing instrumentation; adequacy of GC interfacing is also important.

9.3 MS Ion Sources

9.3.1 Electron Ionization (EI)

The design and efficiency of electron ionization sources is fairly similar among GC-MS manufacturers (Fig. 16). Generally electrons are emitted from a straight tungsten or rhenium wire or an alloy of the two. Electrons are driven from the filament at ca. 70 eV in helical paths along magnetic field lines through the ion chamber to an anode (trap) where they are collected. When ionizable species such as organic compounds in the evacuated source ($< 10^{-4}$ torr) encounter the 70 eV electron beam, about one molecule in 10,000 loses an electron to become charged positively. These ions are drawn out from the ion chamber and accelerated through focussing electrodes, and into the analyzer section where they are to be separated according to their m/e. Since the large majority of positively charged molecules and molecular fragments are singly charged, m/e simply represents the mass of the molecule or fragment. Exceptions are discussed in section 9.4.4 below.

Up to the present time ion sources used for GC-MS apparatus have not differed greatly from those which apply to strictly MS operations. Because of the gas load from the GC (the carrier gas), GC-MS operation differs from many conventional MS operations and in time this may be reflected in sources especially designed for GC-MS work. For example, the present CVC (formerly Bendix) time-of-flight (TOF) mass spectrometer has a source design comparatively "open" to a large vacuum pumping system. Otherwise MS sources have been comparatively "tight" (i.e., gas-tight). As a result, source vacuum pumping overcapacity has received no special attention until the rise of GC-MS.

9.3.2 Chemical Ionization (CI)

Recently, sources have become commercially available for chemical ionization MS. CI operates somewhat like EI in that initial ionization is the result of electron bombardment. However, the source is operated at higher pressure (0.1 to 1 torr). Most of the pressure is due to the

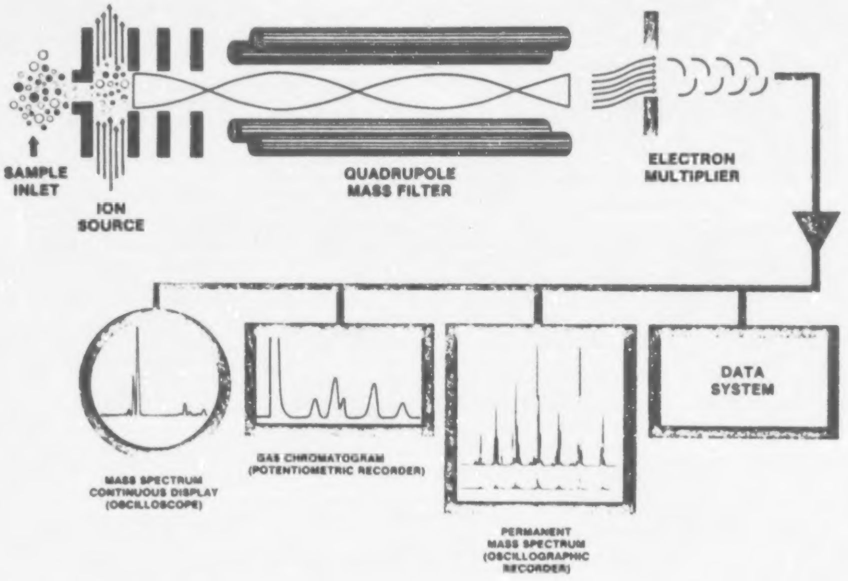

SAMPLE INLET
ION SOURCE
QUADRUPOLE MASS FILTER
ELECTRON MULTIPLIER
DATA SYSTEM
MASS SPECTRUM CONTINUOUS DISPLAY (OSCILLOSCOPE)
GAS CHROMATOGRAM (POTENTIOMETRIC RECORDER)
PERMANENT MASS SPECTRUM (OSCILLOGRAPHIC RECORDER)

Figure 13: Schematic diagram of a quadrupole mass spectrometer. The arrows in the ion source represent 70 eV electrons. The spirals extending from the ion source through the quadrupoles represent sample ion trajectories culminating in the arrows at the electron multiplier (from Ref. 53).

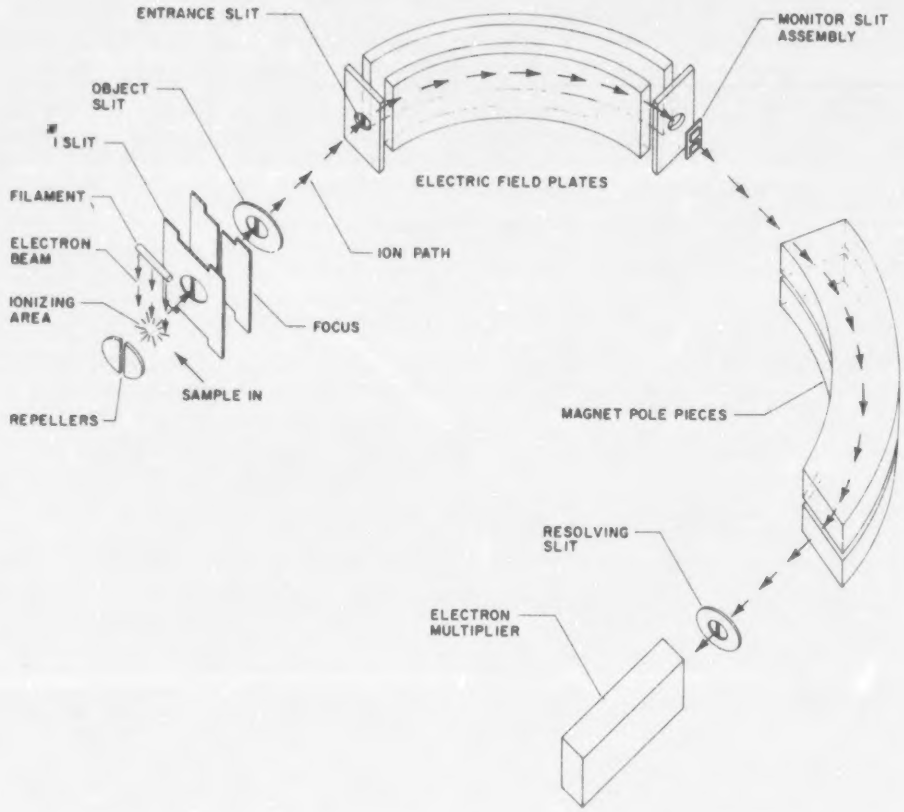

ENTRANCE SLIT
MONITOR SLIT ASSEMBLY
OBJECT SLIT
I SLIT
FILAMENT
ELECTRON BEAM
IONIZING AREA
REPELLERS
SAMPLE IN
FOCUS
ION PATH
ELECTRIC FIELD PLATES
MAGNET POLE PIECES
RESOLVING SLIT
ELECTRON MULTIPLIER

Figure 14: Schematic diagram of a magnetic sector mass spectrometer equipped with an electrostatic sector. The arrows at the filament represent 70eV electrons. The arrows passing through various slits and the electrostatic and magnetic sectors to the electron multiplier represent the sample ion trajectory (from Ref. 54).

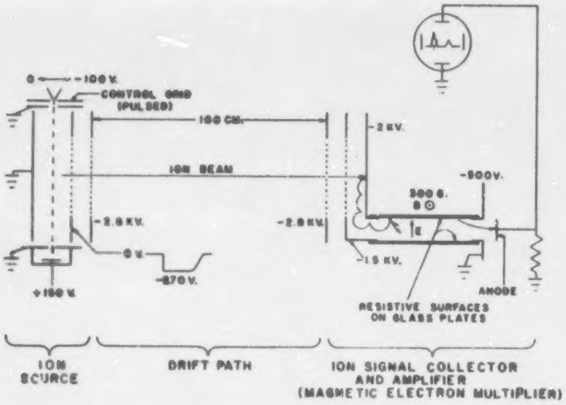


Figure 15: Schematic diagram of a time-of-flight mass spectrometer (from Ref. 55).

deliberate introduction of a reagent gas (or vapor). Initial ionization is almost entirely confined to interaction of the chemical reagent species with the electron beam. The ionized reagent species in turn interacts with the sample, transferring charge and/or atoms to ionize it and produce a CI mass spectrum. Depending on the reagent gas employed, the mass spectrum may bear little or no resemblance to the EI spectrum. Generally, the reagent is chosen for its ability to enhance the upper mass end of the mass spectrum by stabilizing the resultant ionized molecule. Most CI work has used methane as the reagent gas to generate CH_5^+ and $C_2H_5^+$ ions which in turn are used to ionize sample molecules which are too unstable to yield a molecular ion by EI. Other gases have also been employed (e.g., isobutane, nitrogen, hydrogen). Interestingly, when these gases are used as the GC carrier gas, the entire GC effluent can be directly introduced within the CI chamber.

Source pressures of up to 1 torr are maintained by having a very "tight" source chamber which is surrounded by a vacuum system capable of reducing the pressure to less than 10^{-4} torr during GC operation. CI generated sample ions are accelerated electrically through a small orifice into the evacuated analyzer section which is maintained at pressures low enough (ca. 10^{-6} torr) to prevent sensitivity or resolution losses through collisions with residual gases. Normally CI sources require substantially greater pumping capacity than EI sources to handle the reagent gas load. With GC-MS there is also the possibility of high gas loads (depending on the GC-MS interface); however, further additional pumping capacity is not necessary when the carrier gas also serves as the CI reagent gas. Unfortunately, the most widely used GC carrier gas, helium, produces CI spectra which are almost indistinguishable from EI spectra.

9.3.3 MS Ion Source Summary and Conclusions

It is anticipated that EI GC-MS will predominate over CI and other source types for environmental surveys of pesticide residues, where a previously identified spectrum will suffice regardless of lack of molecular ion. CI would be expected to play a back up role, identifying the structure of the more unstable pesticide residues, particularly metabolites. Once identified, these compounds would be surveyed according to their reference EI spectra. Combination EI-CI sources are available from Hewlett-Packard (Fig. 17), Finnigan and DuPont.

9.4 MS Analyzers

Ions generated from organic molecules in the MS source are drawn out of the source and accelerated into the analyzer section by suitable electrostatic fields. The purpose of the analyzer is to separate the positive organic ions (molecular and/or fragment ions) according to their m/e. For GC-MS analysis of pesticide residues this is accomplished by one of three principal types of MS analyzers:

(a) quadrupole
(b) magnetic deflection
(c) time-of-flight (TOF).

The order of listing represents the order of popularity of MS analyzers currently sold for GC-MS use. This also represents a complete reversal of choice during evolution of this technique in the past decade. TOF mass spectrometers were most popular at first, then magnetic, and most recently the quadrupole. The performance of these three principal MS analyzers cannot be compared in every detail; however, at least part of the ascendancy of the quadrupole MS analyzer is due to its lower cost while maintaining performance satisfactory for most low resolution MS applications coupled to GC.

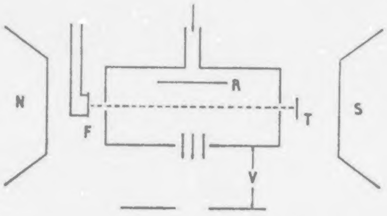


Figure 16: Schematic diagram of a typical electron impact ion source. N,S: north and south poles of electron collimating magnet. F: filament, source of 70 eV electrons. T: trap, collecting anode for electron beam. R: ion repeller. Sample inlet: opening above ion repeller R. V: ion accelerating voltage. Ion exit slit: bottom electrical plate (from Ref. 56).

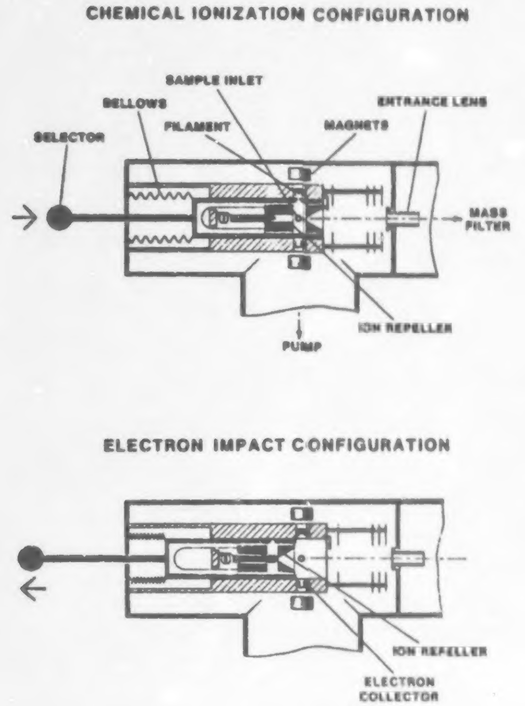


Figure 17: Hewlett Packard combination EI-CI source (from Ref. 57).

9.4.1 Quadrupole MS Analyzers

Quadrupoles belong to a family of MS analyzers which have also been identified as RF-DC mass filters. Physically, the quadrupole consists of an element of four parallel cylindrical metal rods arranged in a rectangular configuration (Fig. 13). Adjacent insulated poles are oppositely charge with a DC voltage upon which a radiofrequency voltage has been superimposed. Variations include the monopole and the dodecapole, a quadrupole with eight trimmer poles (Fig. 18).

Ions entering the quadrupole analyzer longitudinally near the center of the pole cluster travel in a zig-zag pattern according to the RF-DC field parameters. Most ions having the particular m/e for which the instrument is tuned survive lengthwise transit through the oscillating field and contact the electron-multiplier ion collector at the other end for recording of intensity. The intensity is proportional to the ion density at that particular mass/charge ratio. Other ions assume unstable trajectories and collide with the rods or analyzer walls to become discharged and pumped away as neutral molecules.

Although the mathematical description of the principle of operation is complex, a linear relationship exists between the DC voltage applied and the particular mass recorded. Thus, when properly tuned, a linear voltage ramp will produce a linear mass scan. This is an advantage for computer data acquisition and processing, e.g., it facilitates computer control of the MS scan to determine which mass positions should be monitored and for how long. The linear mass scan according to DC voltage is also extremely convenient for manual analog data recording. Other advantages of quadrupole analyzers include rapid mass scanning of GC peaks (e.g., over 300 amu/sec) and convenient size.

Two problems associated with quadrupoles deserve mention. The first is the tendency of the poles to become progressively coated with sample residues with use. The coating is dielectric and can interfere with the electrical fields of the poles. Resolution and mass scale stability may suffer in cases of serious contamination. The eight trimmer poles in the dodecapole configuration help to offset this process but eventually the analyzer must be disassembled and cleaned with a fine abrasive, perhaps 2 to 4 times a year.

The second problem is the discrimination against high-mass molecules compared to magnetic or TOF analyzers. This is explained as due to the more devious trajectories taken by the heavier ions traveling at slower velocities. Fewer survive the longer journey to the ion collector. This problem can be partially overcome by electrically inserting the heavier ions deeper into the analyzer element. The Hewlett-Packard dodecapole instrument accomplishes this with an electrical lens between the source and analyzer programmed according to the mass scan voltage.

9.4.2 Magnetic Deflection MS Analyzers

Magnetic analyzers go back to the origin of mass spectrometry. They are still very widely used in a variety of MS applications and are necessary for high resolution mass spectrometry. Smaller versions are preferred for GC-MS to minimize magnet hysteresis effects for rapid scanning requirements.

Magnetic analyzers operate by the deflection of charged particles moving unimpeded (i.e., under vacuum) through a uniform magnetic field. In a

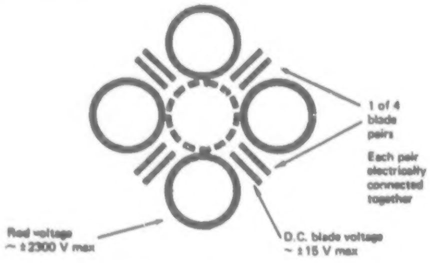

1 of 4 blade pairs
Each pair electrically connected together
Rod voltage ~ ±2300 V max
D.C. blade voltage ~ ±15 V max

Figure 18: Dodecapole analyzer cross section (from Ref. 57).

magnetic analyzer MS of fixed radius (r), the mass/charge ratio (m/e) of an ion which can successfully travel from the source to the ion collector along the flight path of radius (r) is directly proportional to the square of the uniform field strength (H^2) and inversely proportional to the accelerating voltage (V), i.e., $m/e = k\,H^2/V$. Thus a mass spectrum of a sample may be generated by varying (sweeping) either the field strength (H) or the accelerating voltage (V).

Sweeping the accelerating voltage (voltage scanning) is not popular for GC-MS because the higher mass end of the spectrum is reached by a lower accelerating voltage, which results in slower particles and diminished response by the electron multiplier at the collector. In other words, voltage scanning leads to excessive high-mass discrimination. All magnetic analyzers for GC-MS generate a mass spectrum by uniformly sweeping the magnetic field. High resolving power ($m/dm > 10{,}000$) attainable with large, slowly swept magnets has been sacrificed in GC-MS systems in return for scanning speeds (1-3 sec) more appropriate for GC. Even so, mass resolution is generally higher ($m/dm > 1000$) for the smaller magnetic analyzers in GC-MS work than with either quadrupole or TOF analyzers.

Frequently resolution is improved by including an electrostatic analyzer (ESA) in the system. The ESA consists of two concentric electrical field poles (see Fig. 14) which are suitably charged with a DC voltage such that only correctly accelerated ions can enter the magnetic analyzer. This improves resolution by narrowing the energy spread of the ions emerging from the source.

9.4.3 Time-of-Flight MS Analyzers (TOF)

Initially almost all GC-MS work was performed using TOF analysis (see Fig. 15). The principle of operation is relatively straightforward. It is based on the fact that in a vacuum lighter ions of the same charge travel faster than heavier ions when electrically accelerated through a given potential gradient. This difference in velocity according to m/e over a given path length, viz., the distance between the ion source and the ion collector, allows differences in mass to be registered at the ion collector according to their time-of-arrival. Practical considerations limit the length of the analyzer section (flight tube) to about 2 meters. This allows differences of 1 amu to be distinguished up to about 400 amu. During the time that the ions are accelerated down the flight tube, the source is prevented from generating any further ions by a negative voltage on a grid near the filament. The ionizing period of the electron beam is 2 μsec and the flight time about 48 μsec, hence about 20,000 spectra/sec are scanned which is suitable for a very steady oscilloscopic presentation.

Since the TOF scanning rate is fast compared to GC peak duration, the TOF enjoyed initial popularity with on-line GC analysis over the more slowly scanned magnetic instruments of a decade ago. Quadrupoles were then nonexistent. Two disadvantages of TOF mass spectrometers have penalized them in the GC-MS competition:

a) the cumbersome size required for larger than 0-400 amu mass scale (important in biological applications), and

b) the intrinsically lower sensitivity resulting from samples being ionized only 4% of the time (2 μsec out of 50 μsec).

9.4.4 MS Analyzer Comparison and Summary

The TOF analyzer initially was the most widely employed for on-line GC-MS analysis because it was the only MS analyzer which could scan fast enough for narrow GC peaks (e.g., 1 sec scans). The mass range and resolution (unit resolution to 400 amu) were not as great as those attainable on magnetic analyzers, so when smaller, magnetic analyzers with 2-5 sec sweep rates became available, they were preferred in many GC-MS applications. The first quadrupole mass spectrometers became available around 1967 and have moved to the fore with improvements.

Quadrupoles are more compact than either TOF or magnetic analyzers and therefore can be evacuated better. This is important for the gas loads in GC-MS analysis. The quadrupole can be scanned faster than magnetic analyzers currently available (0-350 amu in 1 sec for the Hewlett-Packard dodecapole) and the mass range (0-700 amu) is greater than the TOF. Furthermore, a linear mass scale is produced by a linear voltage sweep. These factors, plus a favorable production cost have led to the predominance of the quadrupole for a great many GC-MS applications. This is especially true where high-volume computer data acquisition and processing is essential.

TOF and magnetic analyzers still maintain certain specialized advantages over the quadrupole. For example, the great scanning speed obtainable with the TOF (20,000 scans/sec) makes it invaluable in studies of fast chemical reaction kinetics in the gas phase, e.g., air pollution chemistry. On the other hand, magnetic analyzers provide information not available on either quadrupoles or TOFs. For example, broad ion peaks may be observed at non-integral mass numbers which are due to ions decomposing after leaving the source. Such ions are termed "metastables" and knowledge of their mass position may be used to calculate the masses of the parent and daughter fragments involved in post-acceleration decompositions. This information may be useful in determining the structure of unidentified molecules, although metastable ion sensitivities are often too low for pesticide residue analysis. Note: the complementary use of an electrostatic analyzer in conjunction with a magnetic analyzer may severely reduce the appearance of metastables in the spectrum.

Magnetic analyzers may be superior to quadrupoles and TOFs in mass range and resolution, but they suffer when it comes to automation. Maintaining mass scale calibration presents difficulties. Since m/e is proportional to the field strength squared (H^2), a Hall-effect probe is needed to determine the field strength. Besides being a significant added expense, this device is adversely affected by minor ambient temperature fluctuations. Early attempts to establish a stable mass scale calibration by operating the magnet sweep (scan) in a precisely timed cyclical mode proved to be unreliable, however this seems to be corrected in the fast-scanning DuPont and Varian GC-MS instruments.

Specific-ion detection (discussed in Section 9.9) is cumbersome with magnetic analyzers. To monitor specific ions in a GC peak, precious time must be spent wading through irrelevant parts of the spectrum as the magnetic field is progressively adjusted from one non-adjacent m/e position to another. Quadrupole or TOF analyzers can skip from one m/e position directly to a non-adjacent m/e position and thus maximize GC sample sensitivity.

9.5 MS Ion Collectors

Once sample ions have been dispersed by the analyzer according to m/e, a means for detecting them is required. For ordinary GC-MS analysis this invariably involves a high gain (10^5 to 10^6) ion collector called a secondary electron multiplier (Fig. 20). High current gain occurs when an energetic sample ion impinges on the sensitized cathode (or first dynode) surface, usually a beryllium copper alloy. This causes a number of secondary electrons to be emitted. In turn these are accelerated to another dynode, releasing further secondary electrons. This process is repeated in cascade fashion through 12 to 16 dynode stages to provide a high sensitivity and rapid response. The final current signal is processed electronically for oscillographic recording or computer data acquisition.

An electron multiplier operating under the constraint of a magnetic field is employed in TOF applications (Fig. 16) because of stricter band-pass requirements. Secondary electron emissivity is attained by a sensitized high-resistance surface on insulating glass. This allows the secondary electrons to move cycloidal paths under the influence of a magnetic field (Fig. 15). Current gain is comparable to electrostatic electron multipliers, above.

9.6 MS Vacuum Systems

Much information is available from vacuum technology monographs and manufacturers' brochures to which the reader is referred. Vacuum systems for GC-MS have evolved steadily in recent years, converging to very similar hardware among manufacturers. For example, GC-MS vacuum diffusion pumps now use a pentameric polyphenyl ether pump fluid in conjunction with Freon refrigerated baffles almost exclusively. In most cases this dispenses with liquid nitrogen or water cooling and is a great convenience. Vacuum pumping capacity is much larger now with standard GC-MS systems; nevertheless, the user should check that the vacuum lines have minimum restriction to flow, i.e., optimum gas conductance. *This means that the inside diameter of piping, the presence of valves, bends and baffles should be evaluated as well as the rated capacity of the vacuum pumps.* Generally, manufacturers can supply this information.

All good GC-MS vacuum systems have protective devices in case of accidents such as a sudden loss of vacuum (venting to atmosphere) or power failure. Vacuum pumping requirements vary according to the type of GC-MS interface employed (see Section 9.7). It is almost always a good idea to have the analyzer section pumped independently from the ion source section, the only opening between the two being the ion exit aperture. This arrangement, known as differential pumping, facilitates high-vacuum integrity in the analyzer and prevents degradation of sensitivity, resolution and mass scale stability.

9.7 GC-MS Interfacing

Properly interfacing a gas chromatograph to a mass spectrometer is one of the most important tasks facing designers of GC-MS systems. The problem is to transfer the sample contained in 20 to 30 ml/min of carrier gas at 1 atm (760 torr) into the MS ion source while maintaining vacuum $< 10^{-6}$ torr. The ideal situation is one in which all the GC carrier gas is pumped off while the entire sample is introduced to the MS. This can be done with separate, off-line GC sample collection and subsequent batch analysis by MS but it is too unwieldy for the complex mixtures of trace (<1 μg) constituents. Hence, to avoid manual sample handling with its concomitant risks of contamination and loss, efficiently coupled GC-MS is highly desirable for trace pesticide residue analysis.

In the past decade strenuous efforts have been devoted to the task of continuously transferring as much separated GC sample component and as little carrier gas as possible to the mass spectrometer. Some devices have been highly sucessful. Others are no longer seriously marketed with new GC-MS systems and will not be discussed here in detail.

9.7.1 Direct Coupling Interface

Direct MS introduction of the entire GC effluent, somewhat paradoxically, is among the earliest and the latest concepts for combining GC separation directly with MS identification. When compared to other types of interfacing, the direct connection has the advantage that the entire GC effluent is utilized. No separation of carrier gas from sample (which may lead to sample loss) is attempted. The added bulk and expense of suitable pumping is a factor to be balanced against the more complete integrity of sample transfer from GC to MS.

Several features of the direct total introduction interface are worthy of mention. First, to maintain a source vacuum $\leq 10^{-4}$ torr with an influx of 20-30 ml/min helium generally requires a diffusion pump rated at about 500 l/sec with an absolute minimum of flow restriction between source and pump. Second, the connection between the GC column and the MS source should be conveniently short and gas-tight. Third, it should be as inert as possible at elevated temperatures (200 to 300°C). Fourth, there should be just enough flow constriction in the GC-MS connecting line to minimize vacuum penetration into the GC column. A slight vacuum (e.g., 500 torr) at the end of the GC column is tolerable with the understanding that absolute GC retention times will be shortened.

Currently, computerized GC-MS instruments commercially available with a functional direct GC-MS interface and adequate pumping include those listed in Table 13.

9.7.2 Jet Separator Interface

The jet diffusion or jet orifice separator is, by all current indications, the most widely desired GC-MS interface. In response to persistent demands, almost all GC-MS manufacturers now offer a single-stage version made of borosilicate (Pyrex) glass suitable for the effluent of GC columns in pesticide residue analysis (20 to 30 ml He/min at 1 atm). Precise data on the design and performance of glass jet separators are not generally available; much of the engineering appears to be empirical.

Briefly, the GC effluent passes through a jet orifice into an evacuated chamber (Fig. 19). As the effluent expands into the vacuum, diffusive separation according to molecular weight occurs. With a very light carrier gas such as helium (Mol. Wt. = 4), diffusion into the surrounding vacuum is much faster than that for pesticide molecules whose molecular weights are generally 50 times greater. As a result the heavier pesticide molecules diffuse less, continuing more in a straight line where they are picked up and transferred to the MS by an intake orifice situated opposite the jet-expansion orifice. Removal of more than 90% of the helium with retention of 80% of pesticide-sized molecules for MS analysis has been suggested. In practical terms, most of the sample can be transferred to the MS along with 2 to 3 ml He/min which most current GC-MS source pumps can handle (200 to 300 l/sec).

The jet-orifice separator, especially the single-stage Pyrex models generally available, possess a number of advantages over other alternatives. First, at substantially lower cost and bulk, a properly constructed glass jet-orifice separator can transfer up to 80% of the organic sample. Second, the exposure to chemically reactive surfaces is minimal, comparable to the direct coupling, and much less than with the porous tube separator (Section 9.7.4). Third, sample transfer from GC to MS can be accomplished without spreading

TABLE 13.

Computerized GC-MS Instruments

Manufacturer	Model	Type
CVC (formerly Bendix)	MA-2	Time-of-flight
Du Pont	21-490	Magnetic
	21-491	Magnetic (double focussing)
Finnigan	1015	Quadrupole
	3000	Quadrupole
Hewlett-Packard	5930A	Quadrupole (dodecapole)
Varian	MAT-111	Magnetic

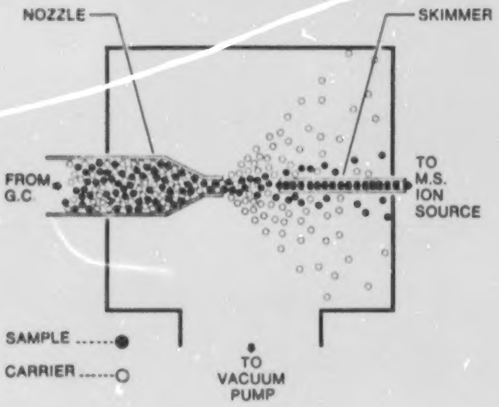


Figure 19: Schematic diagram of jet-orifice separator (from Ref. 58).

or tailing of GC separations as may occur with the silicone membrane separator (Section 9.7.3) or with the porous tube separator. Disadvantages include fragility, a tendency to get plugged with GC column packing granules, and a slight evacuating effect at the GC column terminus. Finnigan, DuPont, CVC (formerly Bendix) and Hewlett-Packard now offer pyrex jet-orifice separators with their GC-MS instrumentation.

9.7.3 Membrane Separator Interface

Membrane separators are offered by a few manufacturers. They employ a thin (0.001 to 0.003"), temperature-resistant, silicone rubber membrane to separate carrier gas molecules from the organics eluting from the GC. Preferential solution of the organics into the silicone membrane allows it to partition the organics from carrier gas. By exposing the back side of the membrane to MS vacuum, the dissolved organic sample can be pumped directly to the MS source for analysis. Most of the helium does not penetrate the membrane but continues out a vent to atmosphere. Sample transfer efficiency is dependent on the nature of the organic molecule and the temperature of operation as well as the residence time in contact with the membrane surface. In practical terms, 20 to 60% organic sample transfer efficiencies are commonplace with 1 to 3 ml helium/min gas load to the MS.

Depending on the physical parameters, the membrane separator in single-stage configuration appears to function about as efficiently as the jet separator. The membrane separator has the advantage of not requiring auxiliary pumping and it is rather simply constructed relatively inexpensively. However, there are several serious limitations. Being made of silicone rubber, it cannot be heated above 220°C without serious deterioration. Temperature further influences two important factors: the solubility of organics in the silicone material, and the porosity of the membrane toward the carrier gas. Each analytical application should be investigated to establish the optimum operating temperature. The most serious disadvantage is the tendency to cause broadening and tailing of GC peaks. This can be ascribed to factors such as the necessity that the membrane have a finite thickness and viscosity to maintain its physical integrity. This means that a finite time is required for organic molecules to dissolve in the rubbery membrane and diffuse across the 0.001 to 0.003 in. thickness separating the GC effluent from the MS. When the temperature is not optimal, serious sample smearing can result.

9.7.4 Porous Tube Separator Interface

The sintered-glass tube of Watson and Biemann has achieved widespread usage and until recently was the standard of the industry. Separation of carrier gas from sample is achieved by the greater effusion of the small helium atoms through the evacuated pores of a hollow, cylindrical sintered-glass frit, as compared to the effusion of heavier organics. Perhaps 10 to 30% of the organic sample proceeds axially along the tubing from the GC into the MS, depending on the tubing porosity and the flow restrictions in the sampling line at either end.

The theory of the porous separator is clear, although there is doubt whether it relates to the real situation. For example, it is difficult to determine the pore size of the sintered frit accurately or if most of the helium is simply removed through a few anomalous holes. Also, flow restriction at the ends of the tube may result more from what is expedient to construct than theory. The most serious shortcoming of this separator is its comparatively large surface area exposed to organic samples at elevated temperatures (150° to 250°C). Serious tailing and complete sample subtraction have been observed (Ref. 59), although silanization of the glass surface may minimize these effects.

9.7.5 Summary

The above interfaces plus simple split valves are the types of GC-MS interfaces that have been offered by GC-MS manufacturers. They have been listed in the general order of their proximity to the ideal of total organic sample transfer from GC to MS without noticeable time delay, decomposition or interference with MS operation. The direct coupling interface with massive source pumping is the closest to this ideal and the most expensive, but not necessarily an extra expense if chemical ionization MS capability is also desired. The other interfaces cost but a fraction of the direct interface. Among these, the single-stage, Pyrex jet separator offers high sample-transfer efficiency (e.g., to 80%) at modest carrier gas load to the MS. Risk of sample decomposition is as low as the direct interface although minor sample discrimination occurs in favor of higher molecular weight compounds, a matter not serious for pesticide residue analysis. The remaining two commercial interfaces have one or more serious shortcomings. The membrane separator must be tested for satisfactory operation for the particular application. GC peak spreading and tailing may be serious. Sample discrimination may occur according to chemical type as well as molecular weight. The porous tube, though improved and miniaturized, may still be comparatively inefficient and chemically reactive toward the samples.

9.8 Computerized GC-MS

The separational capability of gas chromatography combined with the molecular definitiveness of mass spectrometry, affords unparalleled speed, sensitivity, and completeness of identification of organic trace constituents in complex mixtures. The capacity of GC-MS systems to generate detailed data outstrips the ability of technicians to process the data. Hence, automation to acquire, process and display GC-MS data accelerates sample processing and permits analytical personnel to concentrate their efforts on evaluating the data. Computerized data systems are available for most commercial GC-MS systems at a cost roughly comparable to the GC-MS itself. Overall performance depends more upon the versatility and adaptability of the MS analyzer to automation than any other aspect; in effect it is a limiting factor. Otherwise, data acquisition, processing and presentation follows relatively standardized procedures.

MS scans are recorded as electrical intensity (current or voltage) vs. scan voltage, magnetic field strength or time. If these raw data can be converted to *ion relative intensity (rel. int.)* vs. *ion mass/charge ratio (m/e)* files before the next scan is received, significant data storage space is saved. GC-MS data systems should have sufficient capacity to store scans continuously from the start of the gas chromatogram to the end. This means 15 to 20 MS scans/min during a 20 to 30 min gas chromatogram, or up to 600 mass spectra. Since a spectrum may contain more than 100 *m/e* vs. *rel. int.* data points, satisfactory data capacity for one or more continuously scanned GC-MS run is important, as is capability for "in-flight" conversion of raw MS data to mass spectral (i.e., rel. int. vs. m/e) files. Because data storage requirements vary according to type of MS analyzer, it may not be relevant to compare the associated data systems solely in terms of word capacity. More important is the number of MS scans which can be acquired, processed, stored and displayed, and the relative speed and ease of doing so. The design of most commercially available GC-MS software is usually proprietary information.

It is important to be able to subtract one spectrum from another to eliminate anomalies in the sample spectrum due to GC and MS background contamination, e.g., GC column bleed and GC peak overlap. All data systems should feature such a procedure to produce "stripped" spectra. It should also be possible to reconstruct and print out gas chromatograms from MS data files on the basis of the sum of all ion intensities scanned (sometimes denoted "total ionization") or on the basis of the intensity of any specific m/e value. Such reconstructed gas chromatograms are valuable in environmental surveys of pesticide residues, especially specific ion chromatograms (Section 9.9).

Computer control of MS scanning is a significant feature of electrically scanned mass spectrometers (quadrupoles and TOFs). Slaving the MS to the computer permits the following operations:

(a) The MS analyzer may be tuned at the center of the m/e peak until a statistically representative sampling of ions is recorded. This means that the spectrometer can devote more of its scan time at actual mass peak positions. In the normal scan mode more scan time is spent away from the peak top.

(b) As a corollary, a limited number of m/e positions (e.g., a choice of up to 8) may be preselected for MS scanning. By devoting scan time to a few preselected masses, excellent sensitivity and selectivity can be attained for environmental monitoring of trace pesticide residues (see below). Finnigan, DuPont and CVC (formerly Bendix) offer suitable accessories for this purpose.

9.9 Ion Chromatography

The sensitive detection of ions characterizing an organic molecule which has been separated (at least partially) by gas chromatography from a complex matrix makes GC-MS the most powerful technique available for analysis of trace organics in complex mixtures. Many environmental samples are so complex and the compounds of interest so dilute that special ion-monitoring techniques are required to provide the necessary sensitivity and selectivity. By directing the analysis to a few prominent and chemically significant ion signals, improved signal/noise can be achieved in both an electronic sense (improved sample sensitivity) and a chemical sense (greater sample specificity or selectivity).

Ion chromatography is practiced with GC-MS under various names such as specific-ion or multiple-ion detection and mass fragmentography. The first two are accomplished in real time by accessory hardware which programs the mass spectrometer to scan only certain preselected m/e positions. The ion intensities of up to eight m/e values may be recorded directly as chromatograms on strip chart recorders. This technique is useful for trace analyses without computerization or in cases where real-time recording is required. With so-called mass fragmentography the ion chromatograms are reconstructed from processed MS data after completion of the chromatogram. Although more time-consuming, the sensitivity may be comparable to real-time specific-ion detection with quadrupoles and TOFs under control of the computer when the ion statistics are optimized for maximum sensitivity. Otherwise, the only practical difference between real-time and retrospective ion chromatograms is that the former provide a continuous chromatographic plot whereas the latter appear as closely spaced steps. In the average situation, the added expense of the computer for mass fragmentography is well compensated by the added versatility and convenience of automated data processing.

9.10 GC-MS Summary and Conclusions

Commercially available, totally integrated GC-MS computer systems are complex assemblages of instrumentation. Evaluating all the comparative performance characteristics against cost is, therefore, not a simple undertaking and cannot be treated completely herein. Instead, some of the factors relevant to the analysis of trace organic compounds, such as pesticide residues will be highlighted.

The performance of GC-MS data systems are more or less limited by the capability of the mass spectrometer, particularly the analyzer (Section 9.8). The capability of the MS and of its data system can also determine whether highly efficient GC columns (capillaries) can be utilized. In general the commercially available GC-MS-computer systems offer satisfactory gas chromatography for pesticide residue analysis, so the main factors to be considered are the comparative capabilities of (a) GC-MS interfaces and (b) MS analyzers.

At the present time, a well-constructed, *performance-proven* glass (e.g., Pyrex) jet-orifice, helium separator offers the best compromise between cost and efficiency. Performance can and should be stated and guaranteed by the manufacturer. Sample transfer efficiencies up to 80% at MS gas loads of 1 to 2 ml helium/min are possible. To transfer 100% of the sample (along with 20 to 30 ml helium/min), the direct coupling requires a 10 to 15-fold increase in gas pumping capacity. This increases both GC-MS size and cost about 20 to 25% over the glass jet interfaced GC-MS. The membrane separator and the porous tube separator are not currently advised for reasons cited in Sections 9.7 through 9.7.5.

In oversimplified terms the decisive factor in choice of a GC-MS computer system resides with MS analyzer capability. At present the quadrupole maintains the lead but not without compromises. In favor of quadrupoles (including the dodecapole) are:

a) compact size which minimizes pumping requirements and tolerates higher gas loads;
b) scan speeds well suited for GC peaks, e.g., 1 sec;
c) mass scale linearly proportional to voltage;
d) low accelerating voltage which tolerates higher gas loads;
e) rapid scan of individual preselected masses.

However, quadrupoles do not detect metastable ion fragmentation and, unless corrected for, they may exhibit high-mass discrimination.

Magnetic sector and TOF mass spectrometers currently run second to quadrupoles for GC-MS analysis of trace organics. The magnetic analyzer is more difficult and expensive to automate reliably or program for preselected individual ion monitoring. It does, however, reveal metastables. The TOF has two principal disadvantages: a mass range limited to about 400 amu and a 4% duty cycle. On the other hand, larger ion apertures help recover some of the sensitivity lost in the 96% dead time. Also, preselected individual ions may be monitored easily and oscilloscopic mass scan visualization is excellent due to the high frequency of scanning (20,000/sec).

Most current commercial data systems employ conventional small computers having the usual 8 K memory of 12 to 16-bit words. Recently, the faster random access disks have begun to replace tape reels and cassettes for program and data storage. Certainly, much post-chromatography data processing time can be saved this way. Also, welcome relief from the slow, noisy, mechanically troublesome teletypes is being provided by interactive terminals (with CRT) coupled with fast, quiet printers.

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12. PESTICIDE INSTRUMENT NOTES

On the following pages are pesticide analysis Instrument Notes for instruments currently commercially available. All instruments are laboratory type. The descriptor in the mnemonic H20-PES identifies the use as pesticide analysis. The notes are arranged alphabetically by manufacturer and each model has been assigned a number.

The manufacturer's specifications have been published as available, and we gratefully acknowledge that all manufacturers have assisted in the compilation of their notes. All information has been supplied by the manufacturer, either from brochures and instruction manuals or by private communication with the manufacturer. If no information is given for a particular instrument specification, this indicates that none was available. The Instrument Notes should *not* be used as separate entities in themselves. The reader should refer to the discussion preceding the Instrument Notes, the referenced literature, and manufacturers' publications.

12.1. Gas Chromatographs

We have encouraged manufacturers to nominate particular models from their product line which they (and we) believe are best suited for analyzing pesticides. This generally is the least expensive, isothermal, dual glass column, single detector, single amplifier (or electrometer, etc.) gas chromatograph. Ovens suitable for 2-meter, vertical, glass, U-tube columns have been recommended where available. These gas chromatographs also include optional (at additional cost) accessories such as temperature-programming, additional independent detectors, amplifiers, etc. under "Features". Other instruments in a particular manufacturer's product line which offer additional pertinent standard or optional features are noted under "Remarks" near the end of the Instrument Note.

12.2. Integrated Gas Chromatograph/Mass Spectrometer/Data Systems (GC/MS/DS) Systems

Where mass spectral identification and/or quantification of GC peaks is required routinely, the best choice is an integrated GC/MS/DS system: those with the essential features likely to be required for environmental analyses are listed in Table 12.2.

TABLE 12.1. GC INSTRUMENTS
for
LABORATORY ANALYSIS OF PESTICIDES

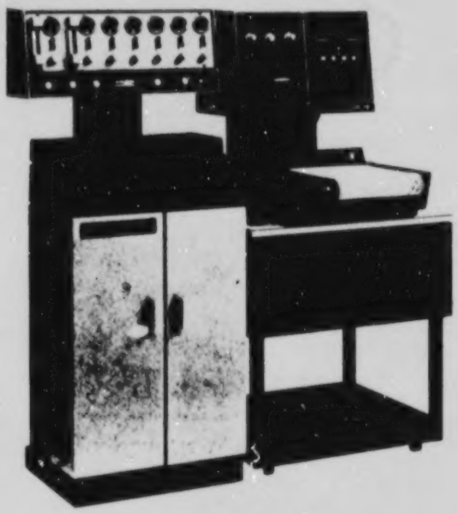
Principle of Operation	Instrument Note	Range	Analysis Time	Cost	Multi-Parameter Capability	Remarks
GC-ECD	~~Beckman 1~~	~~1 ng to 1 pg lindane~~	~~15 to 30 min~~	~~$6,760~~	~~FPD, FID, TCD~~	
"	Bendix 1	"	"	3,550	FPD, FID, TCD	Other Models Available
"	Bendix 3	"	"	5,350	"	"
"	~~Dohrmann 1~~	~~"~~	~~"~~	~~3,925~~	~~MCD, FID, TCD~~	"
"	Fisher 1	0.1 µg to 10 pg lindane	"	4,175	FID, TCD	"
"	Hewlett Packard 3	"	"	3,985	TID, FPD, FID, TCD	"
"	Hewlett Packard 4	"	"	6,595	"	"
"	Packard 1	10 ng to 10 pg lindane	"	3,925	"	"
"	Packard 3	"	"	5,830	"	"
"	Perkin-Elmer 1	"	"	3,550	"	"
"	Tracor 1	1 ng to 1 pg lindane	"	3,540	CCD, FPD, FID, TCD	"
"	Tracor 4	"	"		"	"
"	Varian 1	"	"	3,725	TID, FID	"
"	Varian 3	"	"	6,055	"	"
GC-FPD	Bendix 2	1 µg to 10 pg P; 10 ng to 10 pg S	15 to 30 min.	$4,990	ECD, FID, TCD	Other Models Available
"	Bendix 4	"	"	6,390	"	"
"	Hewlett Packard 1	"	"	6,500	ECD, FID, TID, TCD	"
"	Tracor 2	"	"	4,820	ECD, CCD, FID, TCD	"
"	Tracor 5	"	"	6,500	"	"
GC-MCD	Dohrmann 2	0.1 µg to 0.1 ng lindane		$6,770	ECD, FID, TCD	Other Models Available
"	Dohrmann 3	"	S	6,770	"	"
"	Dohrmann 4	"	N	6,610	"	"
GC-CCD	Tracor 3	0.1 µg to 0.1 ng Cl, N or S		$4,695	ECD, FPD, FID, TCD	Other Models Available
"	Tracor 6	"		6,700	"	"
GC-TID	Hewlett-Packard 2	0.1 µg to 10 pg N & P		$4,160	ECD, FPD, FID, TCD	Other Models Available
"	Perkin-Elmer 2	0.1 µg to 0.1 ng P		3,335	"	"
"	Varian 2	0.1 ng to 0.1 pg P; 10 ng to 10 pg N		2,925	ECD, FID	"
"	Varian 4	"		5,340	"	"

TABLE 12.2. GC/MS/DS INSTRUMENTS
for
LABORATORY ANALYSIS OF PESTICIDES

GC Features	**Du Pont**	**Extranuclear**	**Finnigan**	**Hewlett-Packard**	**Universal Moni[illegible]**
Sample train (except couplings)	Glass	Glass	Glass	Glass	Glass
Temp. program	6 rates	12 rates	11 rates	6 rates	255 rates
Column config.	U-tube	Horiz. coil	U-tube	Vert. coil	Horiz. coil
FID (simultaneous/ alternate with MS)	Option (both)	Option (alt.)	Option (alt.)	Option (both)	Std. (simul.)
GC/MS interface, std. (options)	Glass jet (direct)	Glass jet (none)	Glass jet (direct)	Membrane (jet, direct)	Membrane (none)
MS Features					
Analyzer	Magnet	Quad.	Quad.	Quad.	Quad.
Linear range, amu	43-1000	2-1000 (opt. 1200)	4-800 (opt. 1000)	3-1000	2-400
Max. scan rate, amu/sec.	512	500	500	325	250
Ion source (options)	EI (CI/EI)	EI	EI (CI, CI + EI)	EI (CI/EI)	EI (none)
Direct probe	Option	Option	Std.	Option	None
GC/MS Sensitivity					
Methyl stearate, ng	5	10	5	5	5
S/N, 298 amu (M+)	100/1	3/1	10/1	10/1	> 2/1
GC pk., 1/2-width, sec.	5		5		15 est.
Mass range, amu	43-300	2-1000	4-300	12-300	50-300
Scan rate, amu/sec.	128	100	300	100	50
Resol., dm/m (% h)	1/600 (5%)	1/3000 (50%)	1/1600 (50%)	1/300 (5%)	1/800 (5%)
Data System Features					
Data acquisition/ Interactive modes	Std.	Std.	Std.	Std.	Std.
Terminal	CRT	TTY/CRT	TTY	CRT	TTY
Display	Hardcopier	Hardcopier	Plotter	Hardcopier	TTY
Core memory, bits	128K	96K	128K	256K	192K
Disk memory, bits	24M	24M	24M	2 x 24M	None
Selected ion monit., no. ions (x no. sets)	8	8	4 (x 5)	4 (x 5)	18 (x 16 x 4)
Spectral search	Std. + options	Std. + options	Std. + options	517 pest. + options	16 per GC + options
Model no.	321- 320 (050)	278-7	3200F (003,050,052)- 6100	5981A (minus 006, 007,008)- 5933A (003,005)	Olfax II
Cost	$85,800	$92,550	$88,370	$104,335	$79,200
Manufacturer	Du Pont	Extranuclear	Finnigan	Hewlett-Packard	Universal Monitor
City	Monrovia	Pittsburgh	Sunnyvale	Palo Alto	Pasadena
State, Zip	CA 91016	PA 15238	CA 94086	CA 94304	CA 91107
Area code	(213)	(412)	(408)	(415)	(213)
Telephone	357-2111	782-3884	732-0940	493-1311	351-8877

Halogenated Hydrocarbon Analysis

Gas Chromatograph Model GC 65 (577653)

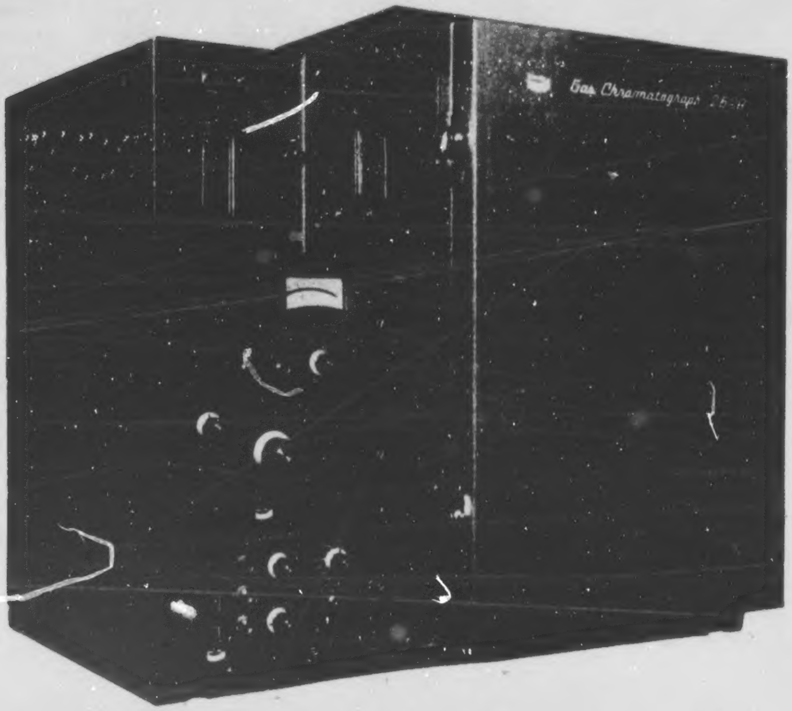


Class	Laboratory: routine analysis/research
Principle of Operation	Gas chromatography - Electron Capture Detection (GC-ECD)
Sensitivity	10^{-12}g lindane ($C_6H_6Cl_6$)
Range	10^{-9} to 10^{-12}g lindane
Interferences	Appreciable interferences from: other halogenated and conjugated unsaturated organic compounds in general, also nitro and cyano groups. Moderate interferences from: oxygenated or nitrogenous organics, O_2, H_2O. Slight or no interferences from: GC column and septum bleed, saturated hydrocarbons and fixed gases, among others.
Multiparameter Capability	Convertible by manufacturer's representative to flame photometric detection (FPD) for phosphorus or sulfur (pesticides); also hydrogen flame ionization detection (FID) for oil analysis, thermal conductivity detection (TCD) for gas analysis (sewage digester gas), helium ionization detector for gas analysis.
Sampling	Method: Syringe injected aliquot of pesticide sample onto glass GC column
Sample Inlet	Type: Silicone rubber septa, spring-loaded, screw-cap retained on fixed stainless-steel injection ports, 1/4" standard; 1/8", 3/16", optional. On-column injection: 1/4" O.D., standard; 1/8", 3/16", optional. Temperature range: Ambient to 425°C Temperature regulation: Fully proportional. ±0.2°C Overheat protection: Fail safe circuitry

Column Oven	Type: Dual columns and injection ports; glass or metal columns, vertical U-tube or coiled; forced air circulation. Carrier gas: He, prepurified Flow control: independent differential flow regulators Flow range, tolerance: 2 to 200 cc/min He, ±0.3% Flow calibration: rotameters calibrated for 20 to 100 cc/min He Column capacity: Standard, 1/4" O.D. glass tubing, 2 ea.: 4' Optional, 1/8" O.D. metal tubing, 2 ea.: 50' Temperature range: Continuously adjustable, ambient to 400°C Temperature regulation: Fully proportional, ±0.04°C Overheat protection: mercury capillary sensor, fully adjustable, ambient to 400° C Temperature program: 30 linear rates; from 0.25 to 3.75 °C/min in 0.25° steps and from 2.5 to 37.5"/min in 2.5° steps. Initial isothermal timer: 0-999.9 min in 0.1/min steps Final isothermal timer: 0 to 999.9 min in 0.1/min steps Cooling rate: 350°C to 50°C in 5 min
Detector	Type: High temperature non-radioactive (helium-discharge) electron capture (ECD) Temperature range: Ambient to 425°C in 25° steps Temperature regulation: Fully proportional, ±0.1°C Accessory gas flow: ca. 40 cc/min prepurified CO_2 Non-linear dynamic range: 10^3
Detector Amplifier	Type: Varactor bridge Sensitivity: 5×10^{-13} A full scale Linear dynamic range: 10^6 Drift: 1×10^{-14} A/day Noise: $\pm 5 \times 10^{-15}$ A maximum Background suppression: 0 to $\pm 10^{-7}$ A with coarse and fine adjustment Attenuation: Input (range), X1, X10, X100, X1000, X10,000; Outout (attenuator), X1, X2, X4, ...X1024 Outputs: For integrator or computer 1, 10 V For recorder 1 mV Time constant: 0.3 sec maximum
Requirements	Recorder: 1 mV, servo-type, strip chart Pressure regulated gas supplies: 0 to 200 psig He; 0 to 100 psig CO_2; all gases, prepurified grade Power: 117 V, 60 Hz (50 Hz optional); 2400 W maximum Size: 140 cm H, 63 cm W, 42 cm D (55-1/4" x 24-3/4" x 16-1/2"), oven console only Weight: 160 kg (350 lb)
Features	Temperature programming is standard
References	Manufacturer's Bulletin 7212
Cost	Gas Chromatograph Model 65(577653) $6,760.
Remarks	Model 65 (577665) ($10,040.) has ECD and FPD (phosphorus or sulfur) capability (single detector amplifier).
Address	Beckman Instruments Inc. 2500 Harbor Boulevard Fullerton, CA 92634 (714) 871-4848

Halogenated Hydrocarbon Analysis

Gas Chromatograph Model 2655(R)-3 (option 06-008A)



Class	Laboratory: routine analysis/research
Principle of Operation	Gas Chromatography - Electron Capture Detection (GC-ECD)
Sensitivity	10^{-12} g lindane ($C_6H_6Cl_6$)
Range	10^{-9} to 10^{-12} g lindane
Interferences	Appreciable interferences from: other halogenated and conjugated unsaturated organic compounds in general, also nitro and cyano groups Moderate interferences from: oxygenated or nitrogenous organics, O_2, H_2O Slight or no interferences from: GC column and septum bleed, saturated hydrocarbons and fixed gases, among others
Multiparameter Capability	Convertible by manufacturer's representative to: flame photometric detection (FPD) for phosphorus or sulfur analysis; flame ionization detection (FID) for oil analysis, thermal conductivity detection (TCD) for gas analysis (sewage digester gas)
Sampling	Method: Syringe injected aliquot of pesticide sample onto glass GC column

Sample Inlet	Type: Silicone rubber septa, screw-cap retained on stainless-steel injection ports 1/4", 1/8", 3/16" sizes standard On-Column Injection: Available in 1/4" Glass Liners (Inserts): Available in 1/4", 1/8", 3/16" sizes Temperature Range: Ambient to 500°C Temperature Regulation: Fully proportional, ±0.5°C Overheat Protection: Line fuse only
Column Oven	Type: Dual columns, injection ports and detectors; glass or metal columns, vertical U-tubes or coiled; forced air circulation Carrier Gas: N_2 Flow Control: Independent differential flow regulators Flow Range, Tolerance: 2 to 200 cc/min He, ±0.3% Flow Calibration: Dual rotameters standard, calibrated for He Column Capacity: Standard, 1/4" O.D. glass tubing, 2 ea.: 3' U tubes 1/4" O.D. metal tubing, 2 ea.: 30' Temperature Range: Continuously adjustable, ambient to 500°C Temperature Regulation: Fully proportional, ±0.5°C Overheat Protection: Variable bimetallic cutoff switch (Optional Temperature Program: 20 linear rates, 0.25, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 16, 20, 24, 28, 32, 36, 40)
Detector	Type: High temperature electron capture (ECD), 15 millicuries Ni^{63} Temperature Range: Ambient to 400°C Temperature Regulation: Fully proportional, ±0.5°C Overheat Protection: Optional bimetallic cutoff switch Accessory Gas Flow: Ca. 40 cc/min Non-linear Dynamic Range: 10^3
Detector Amplifier	Type: Solid state, JFET input design, single differential channel Sensitivity: 1×10^{-12} A full scale Linear Dynamic Range: 10^6 Drift: 1×10^{-13} A/da at constant ambient Noise: Less than 1×10^{-14} A Background Suppression: 0 to $\pm 10^{-11}$, 10^{-8} A with coarse and fine adjustment Attenuation: X1, X10, X100, ...X100,000 Outputs: For 1mV: for integrator or computer 1 V Time Constant: 0.22 sec maximum
Requirements	Recorder: 1 mV, servo-type, strip chart Pressure Regulated Gas Supplies: 0 to 100 psig N_2 Power: 117 V, 60 Hz (220 or 206 V, 50 Hz optional); 3000 W maximum Size: 63.7 cm H, 68.8 cm W, 53.4 cm D (25" x 27" x 21") Weight: 135 kg (300 lb)
References	Manufacturer's catalog 2-72-SM, "Gas Chromatography"
Features	A phosphorous or sulfur flame photometric detector (FPD) and a second independent amplifier are available as options.
Cost	Gas chromatograph model 2655(R)-3 (option 06-008A) $3,550.
Remarks	This column oven is suitable for 2 each 1-m (3') glass U-tube GC columns. A 2-m (6') U-tube column oven with ECD is available (see Bendix 3).
Address	Bendix Corporation, Process Instruments Division Drawer 477 Roncerverte, WV 24970 (304) 647-4358

H2O-PES
Pesticide Analysis
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Phosphorous/Sulfur Analysis

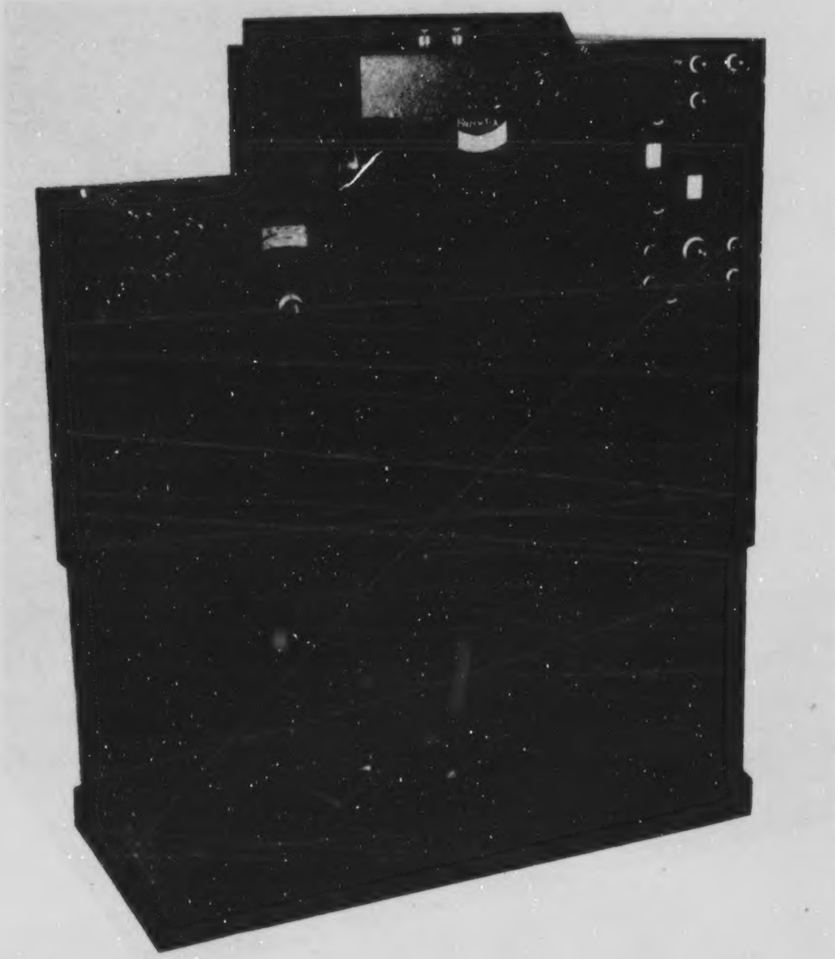
Gas Chromatograph Model 2601-3

Class	Laboratory: routine analysis/research
Principle of Operation	Gas Chromatography - Flame Photometric Detection (GC-FPD)
Sensitivity	10^{-13} g/sec phosphorous; 10^{-12} g/sec sulfur
Range	10^{-7} to 10^{-13} g/sec phosphorus; 10^{-9} to 10^{-12} g/sec sulfur
Interferences	Appreciable interferences from: phosphorus or sulfur containing organic compounds having similar GC retentions Slight or no interferences from: all other substances
Multiparameter Capability	Convertible by manufacturer's representative to: electron capture detection (ECD) for analysis of halogenated hydrocarbons (pesticides); also flame ionization detection (FID) for oil analysis, thermal conductivity detection (TCD) for gas analysis (sewage digester gas)
Sampling	Method: Syringe injected aliquot of pesticide sample onto glass GC column.

Sample Inlet	Type: Silicone rubber septa, screw-cap retained on stainless-steel injection ports 1/4", 1/8", 3/16" sizes standard On-Column Injection: Available in 1/4" Glass Liners (Inserts): Available in 1/4", 1/8", 3/16" sizes Temperature Range: Ambient to 500°C Temperature Regulation: Fully proportional, ±0.5°C Overheat Protection: Line fuse only
Column Oven	Type: Dual columns, injection ports and detectors; glass or metal columns, vertical U-tubes or coiled; forced air circulation Carrier Gas: N_2 Flow Control: Independent differential flow regulators Flow Range, Tolerance: 2 to 200 cc/min He, ±0.3% Flow Calibration: Dual rotameters standard, calibrated for He Column Capacity: Standard, 1/4" O.D. glass tubing, 2 ea." 3' U-tubes 1/4" O.D. metal tubing, 2 ea." 30' Temperature Range: Continuously adjustable, ambient to 500°C Temperature Regulation: Fully proportional, ±0.5°C Overheat Protection: Variable bimetallic cutoff switch (Optional Temperature Program: 20 linear rates, 0.25, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 16, 20, 24, 28, 32, 36, 40)
Detector	Type: phosphorus or sulfur flame photometric (FID) Temperature Range: Ambient to 500°C Temperature Regulation: Fully proportional, ±0.5°C Overheat protection: Optional bimetallic cutoff switch Accessory Gas Flow: Ca. 40 cc/min prepurified H_2; ca. 20 cc/min prepurified O_2, ca. 200 cc/min prepurified air per FID Linear Dynamic Range: 10^5 phosphorus; 10^3 (log) sulfur
Detector Amplifier	Type: Solid state, JFET input design, single differential channel Sensitivity: 1 x 10^{-12} A full scale Linear Dynamic Range: 10^6 Drift: 1 x 10^{-13} A/da at constant ambient Noise: Less than 1 x 10^{-14} A Background Suppression: 0 to ±10^{-11}, 10^{-8} A with coarse and fine adjustment Attenuation: X1, X10, X100, ...X100,000 Outputs: For 1mV: for integrator or computer 1 V Time Constant: 0.22 sec maximum
Requirements	Pressure regulated gas supplies: 0 to 100 psig He; 0 to 30 psig H_2, 0 to 100 psig air; all gases, prepurified grade
References	Manufacturer's catalog 2-72-SM, "Gas Chromatography"
Features	A second independent amplifier and flame photometric detector (EPC) are available for simultaneous sulfur/phosphorous detection at additional cost.
Cost	Gas chromatograph model 2601-3 $4,990.
Remarks	This column oven is suitable for 2 each 1-m (3') glass U-tube GC columns. A 2-m (6') U-tube column oven with FPD is available (see Bendix 4)
Address	Bendix Corporation, Process Instruments Division Drawer 477 Roncerverte, WV 24970 (304) 647-4358

Halogenated Hydrocarbon Analyzer

Gas Chromatograph Model 2555(R)-3 (option-05-009a)



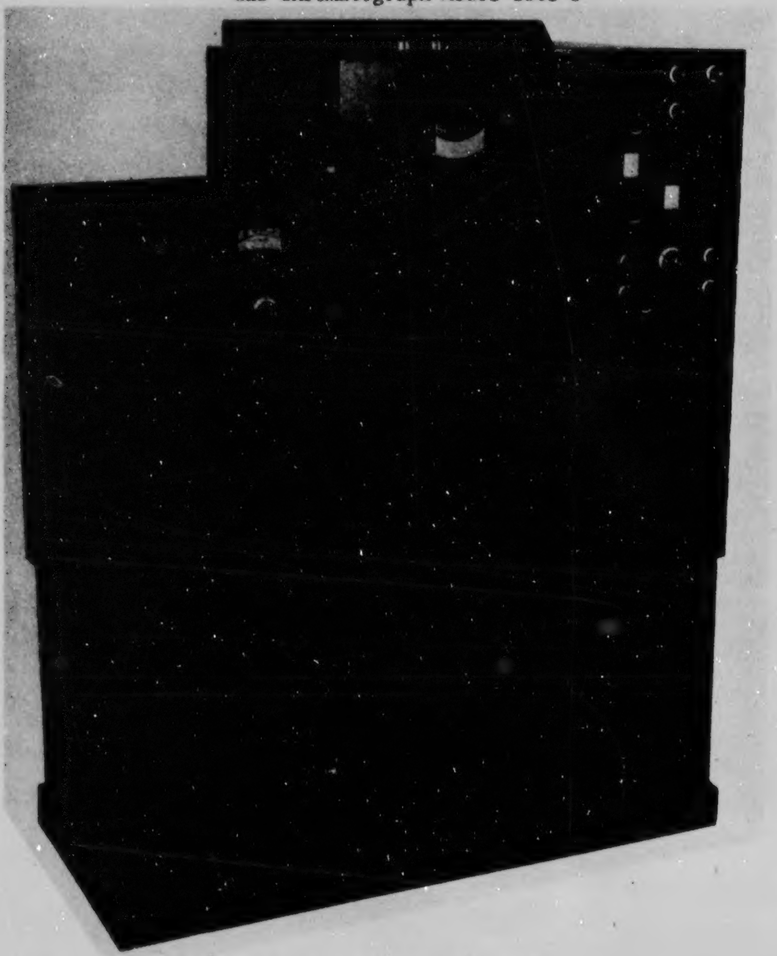
Class	Laboratory: routine analysis/research
Principle of Operation	Gas Chromatography - Electron Capture Detection (GC-ECD)
Sensitivity	10^{-12} g lindane ($C_6H_6Cl_6$)
Range	10^{-9} to 10^{-12} g lindane
Interferences	Appreciable interferences from: other halogenated and conjugated unsaturated organic compounds in general, also nitro and cyano groups Moderate interferences from: oxygenated or nitrogenous organics, O_2, H_2O Slight or no interferences from: GC column and septum bleed, saturated hydrocarbons and fixed gases, among others
Multiparameter Capability	Convertible by manufacturer's representative to: flame photometric detection (FPD) for phosphorus or sulfur analysis; flame ionization detection (FID) for oil analysis, thermal conductivity detection (TCD) for gas analysis (sewage digester gas)
Sampling	Method: Syringe injected aliquot of pesticide sample onto glass GC column

Sample Inlet	Type: Silicone rubber septa, screw-cap retained on stainless-steel injection ports 1/4", 1/8", 3/16" sizes standard On-Column Injection: Available in 1/4" Glass Liners (Inserts): Available in 1/4", 1/8", 3/16" sizes Temperature Range: Ambient to 500°C Temperature Regulation: Fully proportional, ±0.5°C Overheat Protection: Line fuse only
Column Oven	Type: Dual columns, injection ports and detectors; glass or metal columns, vertical U-tubes or coiled; forced air circulation Carrier Gas: N_2 or 10% methane in argon Flow Control: Independent differential flow regulators Flow Range, Tolerance: 2 to 200 cc/min He, ±0.3% Flow Calibration: Dual rotameters standard, calibrated for He Column Capacity: Standard, 1/4" O.D. glass tubing, 2 ea.: 6' U tubes Optional, 1/4" O.D. metal tubing, 4 ea.: 6' U tubes Temperature Range: Continuously adjustable, ambient to 500°C Temperature Regulation: Fully proportional, ±0.5°C Overheat Protection: Variable bimetallic cutoff switch Optional Temperature Program: 20 linear rates, 0.25, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 16, 20, 24, 28, 32, 36, 40)
Detector	Type: High temperature electron capture (ECD), 15 millicuries Ni^{63} Temperature Range: Ambient to 400°C Temperature Regulation: Fully proportional, ±0.5°C Overheat Protection: Optional bimetallic cutoff switch Accessory Gas Flow: Ca. 40 cc/min Non-linear Dynamic Range: 10^3
Detector Amplifier	Type: Solid state, JFET input design, single differential channel, dual channel optional Sensitivity: 1×10^{-12} A full scale Linear Dynamic Range: 10^6 Drift: 1×10^{-13} A/da at constant ambient Noise: Less than 1×10^{-14} A Background Suppression: 0 to $\pm 10^{-11}$, 10^{-8} A with coarse and fine adjustment Attenuation: X1, X10, X100, ...X100,000 Outputs: For 1mV: for integrator or computer 1 V Time Constant: 0.22 sec maximum
Requirements	Recorder: 1 mV, servo-type, strip chart Pressure Regulated Gas Supplies: 0 to 100 psig N_2 Power: 220 V, 60 Hz (50 Hz optional); 6600 W maximum Size: 165 cm H, 86.5 cm W, 53.4 cm D (65" x 34" x 21") Weight: 202 kg (450 lb)
References	Manufacturer's catalog 2-72-SM, "Gas Chromatography"
Features	This model accomodates 2 standard 2-m (6') glass U-tube columns. A phosphorous flame photometric detector (FPD) and a second independent amplifier are available as options.
Cost	Gas chromatograph model 2555(R)-3 (option 05-009a) $5,350.
Remarks	Combination ECD and phosphorous or sulfur FPD (Model 2558R) costs $7990.
Address	Bendix Corporation, Process Instruments Division Drawer 477 Roncerverte, WV 24970 (304) 647-4358

H2O-PES
Pesticide Analysis
Bendix 4
October 1973

Phosphorus/Sulfur Analyzer

Gas Chromatograph Model 2501-3

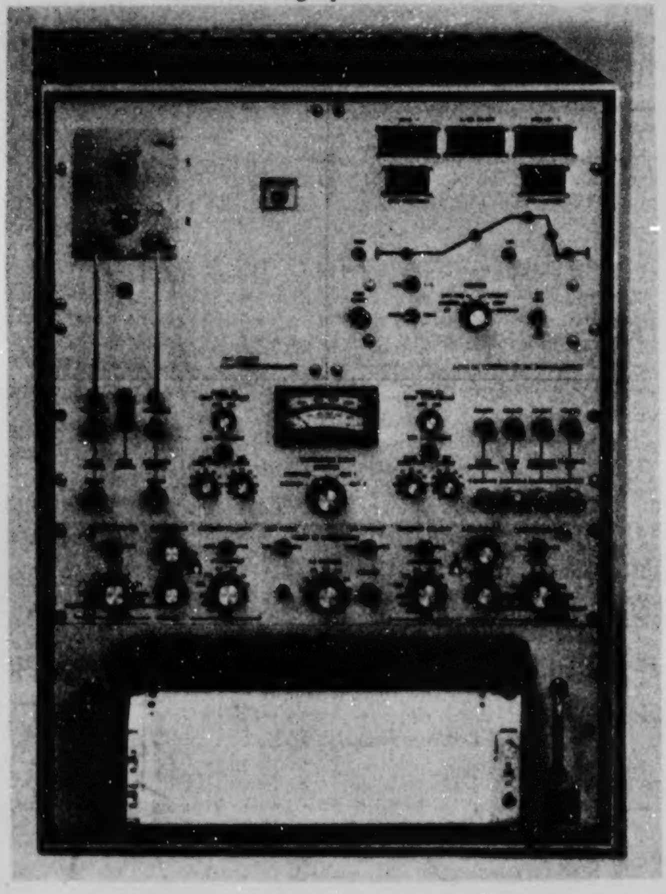


Class	Laboratory: routine analysis/research
Principle of Operation	Gas Chromatography - Flame Photometric Detection (GC-FPD)
Sensitivity	10^{-13} g/sec phosphorous; 10^{-12} g/sec sulfur
Range	10^{-7} to 10^{-13} g/sec phosphorus; 10^{-9} to 10^{-12} g/sec sulfur
Interferences	Appreciable interferences from: phosphorus or sulfur containing organic compounds having similar GC retentions Slight or no interferences from: all other substances
Multiparameter Capability	Convertible by manufacturer's representative to: electron capture detection (ECD) for analysis of halogenated hydrocarbons (pesticides); also flame ionization detection (FID) for oil analysis, thermal conductivity detection (TCD) for gas analysis (sewage digester gas)

Sampling	Method: Syringe injected aliquot of pesticide sample onto glass GC column
Sample Inlet	Type: Silicone rubber septa, screw-cap retained on stainless-steel injection ports 1/4", 1/8", 3/16" sizes standard On-Column Injection: Available in 1/4" Glass Liners (Inserts): Available in 1/4", 1/8", 3/16" sizes Temperature Range: Ambient to 500°C Temperature Regulation: Fully proportional, ±0.5°C Overheat Protection: Line fuse only
Column Oven	Type: Dual columns, injection ports and detectors; glass or metal columns, vertical U-tubes or coiled; forced air circulation Carrier Gas: N_2 Flow Control: Independent differential flow regulators Flow Range, Tolerance: 2 to 200 cc/min He, ±0.4% Flow Calibration: Dual rotameters standard, calibrated for He Column Capacity: Standard, 1/4" O.D. glass tubing, 2 ea." 3' U-tubes Optional, 1/4" O.D. metal tubing, 2 ea." 30' Temperature Range: Continuously adjustable, ambient to 500°C Temperature Regulation: Fully proportional, ±0.5°C Overheat Protection: Variable bimetallic cutoff switch (Optional Temperature Program: 20 linear rates, 0.25, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 16, 20, 24, 28, 32, 36, 40)
Detector	Type: phosphorus or sulfur flame photometric (FID) Temperature Range: Ambient to 500°C Temperature Regulation: Fully proportional, ±0.5°C Overheat Protection: Optional bimetallic cutoff switch Accessory Gas Flow: Ca. 40 cc/min prepurified H_2; ca. 20 cc/min prepurified O_2; ca. 200 cc/min prepurified air per FID Linear Dynamic Range: 10^5 phosphorus; 10^3 (log) sulfur
Detector Amplifier	Type: Solid state, JFET input design, single differential channel, dual channel optional Sensitivity: 1×10^{-12} A full scale Linear Dynamic Range: 10^6. Drift: 1×10^{-13} A/da at constant ambient Noise: Less than 1×10^{-14} A Background Suppression: 0 to $\pm 10^{-11}$, 10^{-8} A with coarse and fine adjustment Attenuation: X1, X10, X100, ...X100,000 Outputs: For 1mV: for integrator or computer 1 V Time Constant: 0.22 sec maximum
Requirements	Pressure regulated gas supplies: 0 to 100 psig He; 0 to 30 psig H_2; 0 to 100 psig air; all gases, prepurified grade
References	Manufacturer's catalog 2-72-5M, "Gas Chromatography"
Features	This model accomodates 2 standard 2-m (6') glass U-tube columns. A second independent amplifier and flame photometric detector (FPD) are available for simultaneous sulfur/phosphorous detection at additional cost.
Cost	Gas chromatograph model 2501-2 $6,390.
Remarks	Dual phosphorus and sulfur FPD is available (Model 2502) for $7,540. Dual phosphorus and sulfur FPD plus ECD is available (Model 2559R) for $8,690.; this includes three electrometers and four injections ports and flow controller.
Address	Bendix Corporation, Process Instruments Division Drawer 477 Roncerverte, WV 24970 (304) 647-4358

Halogenated Hydrocarbon Analyzer (Electron Capture)

Gas Chromatograph Model 2465-E

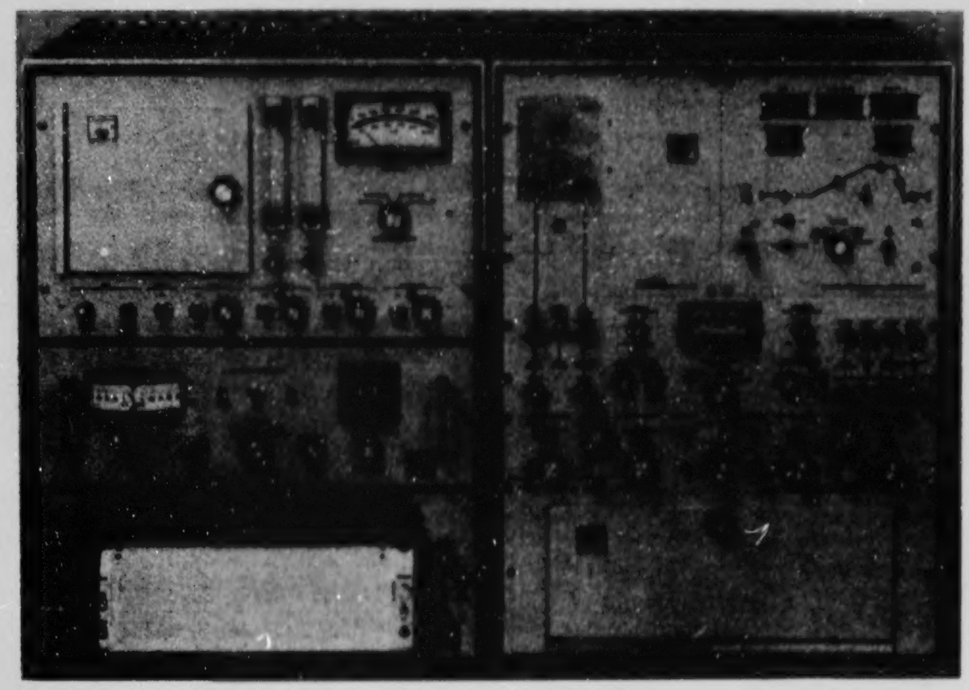


Class	Laboratory: Routine analysis/research
Principle of Operation	Gas Chromatography - Electron Capture Detection (GC-ECD)
Sensitivity	10^{-12} g, lindane ($C_6H_6Cl_6$)
Range	10^{-9} to 10^{-12} g lindane
Interferences	Appreciable interferences from: other halogenated and conjugated unsaturated organic compounds in general, also nitro and cyano groups Moderate interferences from: oxygenated or nitrogenous organics, O_2, H_2O Slight or no interferences from: GC column and septum bleed, saturated hydrocarbons and fixed gases, among others
Multiparameter Capability	Convertible by manufacturer's representative to flame ionization detection (FID) for oil analysis; factory convertible to thermal conductivity detection (TCD) for gas analysis (sewage digester gas), coulometric nitrogen or halogen detector (pesticides), coulometric sulfur detector (petroleum, pesticides)
Sampling	Method: Syringe injected aliquot of pesticide sample onto glass GC column

Sample Inlet	Type: Silicone rubber septa, screw-cap retained on stainless-steel injection ports, 1/8" or 1/4" sizes On-column injection: Available in 1/8" or 1/4" sizes Temperature range: Continuously adjustable 40° to 400°C Temperature regulation: Fully proportional, ±0.1°C Overheat protection: Line fuse only
Column Oven	Type: Dual columns and injection ports; glass or metal columns, horizontally coiled; forced air circulation; low thermal mass Carrier gas: N_2 prepurified Flow control: independent differential flow regulators Flow range, tolerance: 2 to 200 cc/min; ±0.3% Flow calibration: soap bubble flowmeter via calibration divert valves Column capacity: Standard, 1/4" O.D. glass tubing, 2 ea.: 6' Optional, 1/4" O.D. metal tubing, 2 ea.: 20' Temperature range: Continuously adjustable, ambient to 499°C Temperature regulation: Fully proportional, ±0.05°C Overheat protection: Adjustable bimetallic overtemperature limit switch **Optional temperature program: 300 linear rates, from 0 to 29.9°C/min in 0.1° steps**
Detector	Type: High temperature concentric electron capture, 5 millicuries Ni^{63} Temperature range: Ambient to 500°C Temperature regulation: Fully proportional, ±0.1°C Overheat protection: Available option (same as for column oven) Accessory gas flow: Not mandatory Non-linear dynamic range: 10^3
Detector Amplifier	Type: Solid state, parametric design, single channel Sensitivity: 1×10^{-12} A full scale Linear dynamic range: Greater than 2.5×10^5 on input X1; greater than 2.5×10^6 on all other ranges Drift: Less than 2%/da @ constant ambient Noise: 1×10^{-14} A with cables connected Background suppression: 0 to ± 9×10^{-11} A with coarse and fine adjustment, low background; 1000X higher for high background Attenuation: Input (range), X1, X100, X10, X10,000 Output (attenuator, X1, X2, X4, ... X1024 Outputs: For recorder, 1 mV; for computer, 11 V Time constant: 0.15 sec maximum
Requirements	Recorder: 1 mV, servo-type, strip chart Pressure regulated gas supplies: 0 to 100 psig N_2, prepurified grade Power: 115 V, 60 Hz (200 V, 50 Hz optional); 2200 W maximum Size: 68.6 cm H, 50.9 cm W, 45.8 cm D (27" x 20" x 18") Weight: 58.8 kg (130 lb)
References	a) Manufacturer's Bulletin No. SM-481-5/72/10M b) Manufacturer's Pricing Guide No. SM-667-11/71/2M
Features	Concentric ECD design permits non-pulsed operation with N_2 carrier gas
Cost	Gas Chromatograph Model 2465-E $3,925.
Remarks	
Address	Dohrmann Division of Envirotech Corporation 1062 Linda Vista Avenue Mountain View, CA 94040 (415) 968-9710 Telex 345 538 Cable DOHRMANN

Halogenated Hydrocarbon Analyzer (Microcoulometric)

Gas Chromatograph Model 2465 with GTS-20 Halogen Detector

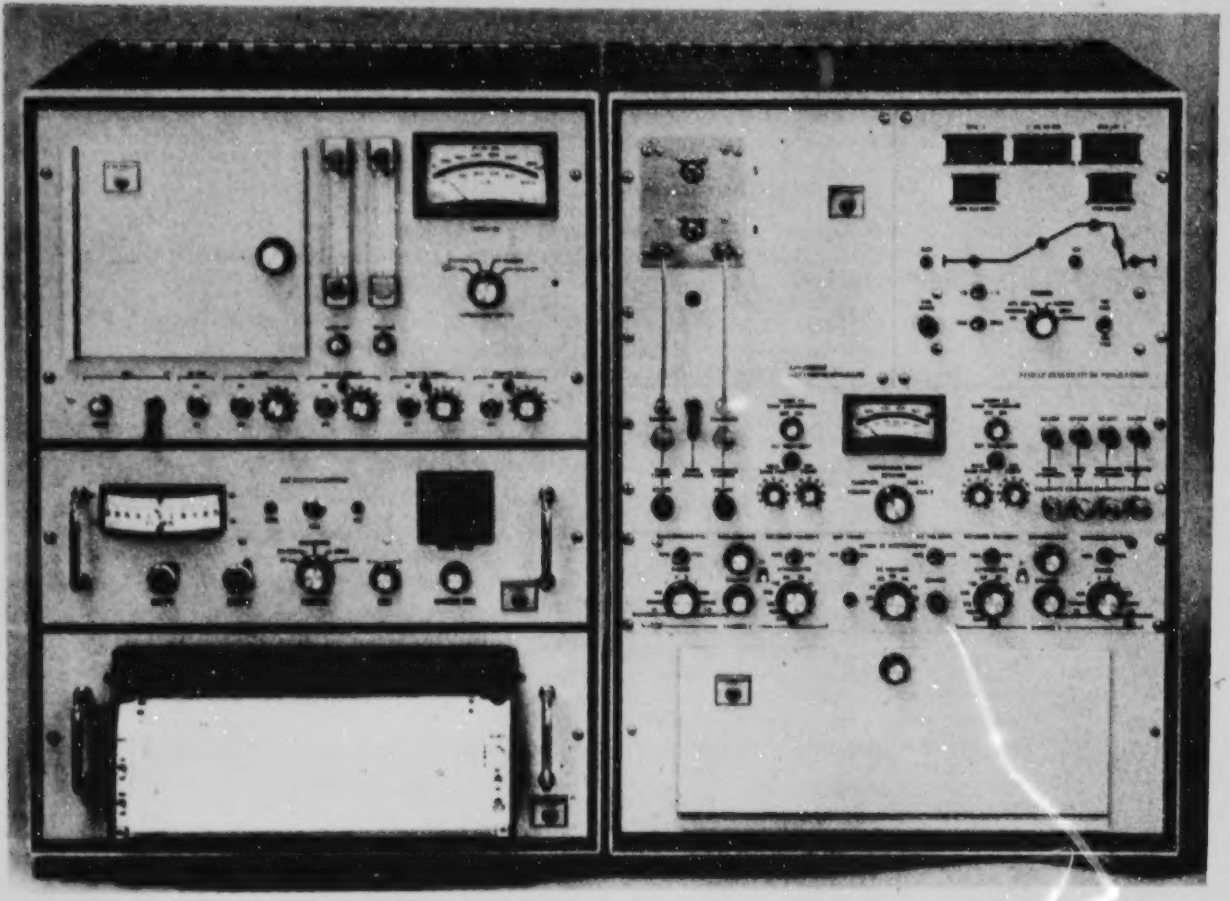


Class	Laboratory: Routine analysis/research
Principle of Operation	Microcoulometric Detection (GC-MCD) for Halogens
Sensitivity	10^{-10} g lindane ($C_6H_6Cl_6$)
Range	10^{-7} to 10^{-10} g lindane
Interferences	Appreciable interferences: None Moderate interferences: None Slight or no interferences: Phosphorus, sulfur, nitrogen
Multiparameter Capability	Convertible to sulfur or nitrogen microcoulometric detection; also electron capture detection (ECD) for pesticide analysis, flame ionization detection (FID) for oil analysis, thermal conductivity detection (TCD) for gas analysis
Sampling	Method: Syringe injected aliquot of pesticide sample onto glass GC column
Sample Inlet	Type: Silicone rubber septa, screw-cap retained on stainless-steel injection ports, 1/8" or 1/4" sizes On-column injection: Available in 1/8" or 1/4" sizes Glass liners (inserts): Available in 1/8" or 1/4" sizes Temperature range: Continuously adjustable, 40° to 400°C Temperature regulation: Fully proportional, ±0.1°C Overheat protection: Line fuse only

Column Oven	Type: Dual columns, injection ports and detectors; glass or metal columns, horizontally coiled; forced air circulation; low thermal mass Carrier gas: He or N_2 prepurified Flow control: independent differential flow regulators Flow range, tolerance: 2 to 200 cc/min He; ±0.3% Flow calibration: soap bubble flowmeter via calibration divert valves Column capacity: Standard, 1/4" O.D. glass tubing, 2 ea.: 6' Optional, 1/4" O.D. metal tubing, 2 ea.: 20' Temperature range: Continuously adjustable, ambient to 499°C Temperature regulation: Fully proportional, ±0.05°C Overheat protection: Adjustable bimetallic overtemperature limit switch (Optional temperature program: 300 linear rates, from 0 to 29.9°C/min in 0.1° steps)
Detector	Type: Microcoulometric Detection (MCD) specific for halogens (Cl, Br, I) Temperature range: transfer line to furnace, continuously adjustable 40° to 400°C Overheat protection: available option (same as for column oven) Accessory gas flow: ca. 100 cc/min prepurified O_2 Linear dynamic range: 10^3
Detector Amplifier	Type: Solid state, microcoulometric design Sensitivity: 10^{-6} A full scale Linear dynamic range: 10^3 Drift: Less than 4%/da @ constant ambient Noise: 2 x 10^{-8} A with cables connected Background suppression: not applicable Attenuation: Output (Range) 1, 2, 3, ... 1000 in steps of 1 Outputs: For recorder, 1 mV Time constant:
Requirements	Recorder: 1 mV, servo-type, strip chart Pressure regulated gas supplies: 0 to 100 psig He; 0 to 100 psig O_2; all gases, prepurified grade Power: 115 V, 60 Hz (200 V, 50 Hz optional); 2200 W maximum Size: 68.6 cm H, 101.8 cm W, 45.8 cm D (27" x 40" x 18") Weight 117.6 kg (260 lb)
References	a) Manufacturer's Bulletin No. SM-557-9/71/1M b) Manufacturer's Technical Reprint No. AI-29
Features	Modular substitution of cell and pyrolysis tubes converts this detector to sulfur or nitrogen detection capability
Cost	Gas Chromatograph Model 2465 with GTS-20 Halogen Detector $6,770.
Remarks	Conversion kits to sulfur or nitrogen detection capability cost $775. and $910., respectively
Address	Dohrmann Division of Envirotech Corporation 1062 Linda Vista Avenue Mountain View, CA 94040 (415) 968-9710 Telex 345 538 Cable DOHRMANN

Sulfur or Nitrogen Analyzer

Gas Chromatograph Model 2465 with GTS-30 or GTS-10 detector



Class	Laboratory: Routine analysis/research
Principle of Operation	Microcoulometric Detection (GC-FID) for sulfur or nitrogen
Sensitivity	10^{-11} g/sec for either sulfur or nitrogen
Range	10^{-8} to 10^{-11} g/sec for either sulfur or nitrogen
Interferences	Appreciable interferences: none Moderate interferences: none Slight or no interferences: Halogen, phosphorus (nitrogen and sulfur)
Multiparameter Capability	Convertible by manufacturer's representative to coulometric halogen detector (pesticides), electron capture detection (ECD) for analysis of halogenated hydrocarbons (pesticides), flame ionization detection (FID) for oil analysis, thermal conductivity detection (TCD) for gas analysis (sewage digester gas).
Sampling	Method: Syring injected aliquot of pesticide sample onto glass GC column

Sample Inlet

Type: Silicone rubber septa, screw-cap retained on stainless-steel injection ports, 1/8" or 1/4" sizes
On-column injection: Available in 1/8" or 1/4" sizes
Glass liners (inserts): Available in 1/8" or 1/4" sizes
Temperature range: Continuously adjustable, 40° to 400°C
Temperature regulation: Fully proportional, ±0.1°C
Overheat protection: Line fuse only

Column Oven

Type: Dual columns, injection ports and detectors; glass or metal columns, horizontally coiled; forced air circulation; low thermal mass

Carrier gas: He prepurified
  Flow control: independent differential flow regulators
  Flow range, tolerance: 2 to 200 cc/min He; ±0.3%
  Flow calibration: soap bubble flowmeter via calibration divert valves
Column capacity:
  Standard, 1/4" O.D. glass tubing, 2 ea.: 6'
  Optional, 1/4" O.D. metal tubing, 2 ea.: 20'
Temperature range: Continuously adjustable, ambient to 499°C
Temperature regulation: Fully proportional, ±0.05°C
Overheat protection: Adjustable bimetallic overtemperature limit switch
(Optional temperature program: 300 linear rates, from 0 to 29.9°C/min in 0.1° steps)

Detector

Type: Microcoulometric Detection (MCD) specific for sulfur (GTS-30) or nitrogen (GTS-10)

Detector Amplifier

Type: Solid state, microcoulometric design
Sensitivity: 10^{-6} A full scale
Linear dynamic range: 10^{3}
Drift: Less than 4%/da @ constant ambient
Noise: 2×10^{-8} A with cables connected
Background suppression: not applicable
Attenuation: Output (Range) 1, 2, 3, ...1000 in steps of 1
Outputs: For recorder, 1 mV
Time constant:

Requirements

Recorder: 1 mV, servo-type, strip chart
Pressure regulated gas supplies: 0 to 100 psig He; 0 to 100 psig O_2; all gases, prepurified grade
Power: 115 V, 60 Hz (200 V, 50 Hz optional); 2200 W maximum
Size: 68.6 cm H, 101.8 cm W, 45.8 cm D (27" x 40" x 18")
Weight: 117.6 ke (260 lb)

References

a) Manufacturer's Bulletin No. SM-664-10/71/1M
b) Manufacturer's Bulletin No.

Cost

Gas Chromatograph Model 2465 with GTS-30 detector (sulfur)	$6,770.
Gas Chromatograph Model 2465 with GTS-10 detector (nitrogen)	$6,610.

Remarks

Address

Dohrmann
Division of Envirotech Corporation
1062 Linda Vista Avenue
Mountain View, CA 94040
(415) 968-9710   Telex 345 538   Cable DOHRMANN

H2O-PES
Pesticide Analysis
Fisher 1
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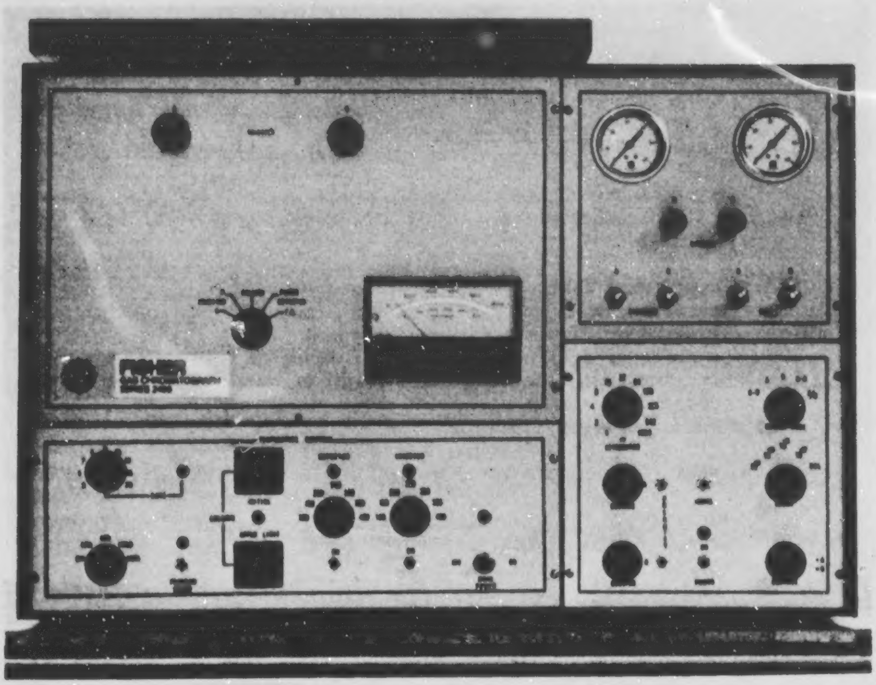
Halogenated Hydrocarbon Analyzer

Gas Chromatograph Model 2400-001



Class	Laboratory: Routine analysis/research
Principle of Operation	Gas Chromatography - Flame Ionization Detection (GC-FID)
Sensitivity	10^{-11} g lindane ($C_6H_6Cl_6$)
Range	10^{-7} to 10^{-11} g lindane
Interferences	Appreciable interferences from: other halogenated and conjugated unsaturated organic compounds in general, also nitro and cyano groups Moderate interferences from: oxygenated or nitrogenous organics, O_2, H_2O Slight or no interferences from: GC column and septum bleed, saturated hydrocarbons and fixed gases, among others
Multiparameter Capability	Convertible by manufacturer's representative to flame ionization detection (FID) for analysis of oil; thermal conductivity detection (TCD) for gas analysis (sewage digester gas)
Sampling	Method: Syringe injected aliquot of pesticide sample onto glass GC column
Sampling Inlet	Type: Silicone rubber septa, screw-cap retained on stainless-steel injection ports, 1/8" or 1/4" size On-column injection: in 1/4" size Glass liners (inserts): Available in 1/4" size only Temperature range: 50° to 400°C in 50° steps Temperature regulation: Fully proportional, ± °C Overheat protection: Line fuse only

Column Oven	Type: Dual columns and injection ports, glass or metal columns, vertically coiled; thermostatted, forced air circulation Carrier gas: N_2 prepurified Flow control: independent differential flow regulators Flow range, tolerance: 2 to 200 cc/min, ±0.3% Flow calibration: soap bubble flowmeter Column capacity: 1/4" O.D. glass tubing, 2 ea.: 6' standard 1/4" O.D. metal tubing, 2 ea.: 50' Temperature range: Continuously adjustable, ambient to 400°C Temperature regulation: Fully proportional, ±0.5°C Overheat protection: 400°C cut-off, fusible metal strip and adjustable thermostat Optional temperature program: 9 linear rates, 0.5, 1, 2, 4, 8, 10, 12, 15, 20 °/min
Detector	Type: High temperature electron capture (ECD) 15 or 30 millicuries Ni^{63} Temperature range: 50 to 400°C, in 50° steps Temperature regulation: Fully proportional, ± °C Overheat protection: Fuse 10% methane in argon Accessory gas flow: ca. 100 cc/min prepurified H_2; ca. 300 cc/min prepurified air per FID Linear dynamic range: 10^6
Detector Amplifier	Type: JFET, temperature compensated, log linearizer, pulser Sensitivity: 1 x 10^{-12} A full scale Linear dynamic range: 10^6 Drift: 0.3%/hr at constant ambient Noise: 1.5% peak to peak at maximum sensitivity with cable disconnected Background suppression: 0 to ±10^{-7} A with coarse and fine adjustment Attenuation: Input (range), X1, X10, X100, X1,000 Output (attenuator),X1, X2, X4, ...X1024 Outputs: For recorder, 1 mV Time constant: 0.3 sec maximum
Requirements	Pressure regulated gas supplies: 0 to 100 psig N_2, prepurified grade Power: 117 V, 60 Hz (220 V, 50 Hz optional; 3000 W maximum Size: 40.7 cm H, 61 cm W, 57.1 cm D (16" x 24" x 22-1/2") Weight: 61.3 kg (135 lb)
References	a) Manufacturer's Bulletin No. 267A 11-240-100
Features	ECD log output is linearized for greater sensitivity
Cost	Gas chromatograph model 2400-001 $4,175.
Remarks	Model 4800-001 ($6,500.) has expanded temperature programmer, multiple detector capabilities, and accessory gas rotameters
Address	Analytical Instrument Division Fisher Scientific Company 711 Forbes Avenue Pittsburgh, PA 15219 (412) 562-8300 Telex 86839

H2O-PES
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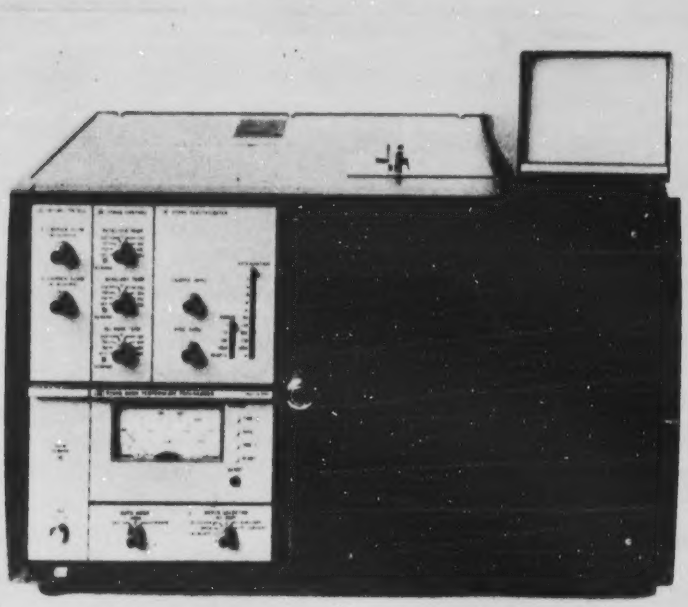
Phosphorus/Sulfur Analyzer

Gas Chromatograph Model 5715A (option-005-011-017)



Class	Laboratory: Routine analysis/research
Principle of Operation	Gas Chromatography - Flame Photometric Detection (GC-FPD)
Sensitivity	10^{-11}g phosphorus or sulfur
Range	10^{-6} to 10^{-11}g phosphorus; 10^{-8} to 10^{-11}g sulfur
Interferences	Appreciable interferences from: phosphorus or sulfur containing organic compounds having similar GC retentions Slight or no interferences from: all other substances
Multiparameter Capability	Convertible by manufacturer's representative to electron capture detection (ECD) for analysis of halogenated hydrocarbons (pesticides), thermionic detection (TID) for nitrogen/phosphorus analysis (pesticides); also flame ionization detection (FID) for oil analysis, thermal conductivity detection (TCD) for gas analysis (sewage digester gas).
Sampling	Method: Syringe injected aliquot of pesticide sample onto glass GC column
Sample Inlet	Type: Silicone rubber septa, screw-cap retained on stainless-steel injection ports, 1/8" or 1/4" sizes On-column injection: 1/8" and 1/4" sizes Glass Liners (inserts): 1/8" and 1/4" sizes Temperature range: 100° to 400°C in 50° steps Temperature regulation: Fully proportional, ±0.5°C Overheat protection: fail-safe circuitry, line fuse

Column Oven

Type: Dual columns and injection ports; glass or metal columns, vertically coiled; forced air circulation
Carrier gas: N_2, prepurified
Flow control: independent differential flow regulators;
Flow range, tolerance: 2 to 200 cc/min He, ±0.3%
Flow calibration: soap bubble flowmeter
Column capacity:
1/8" O.D. glass tubing, 2 ea.: 30'
1/4" O.D. glass tubing, 2 ea.: 15'
Temperature range: Continuously adjustable, ambient to 400°C
Temperature regulation: Fully proportional, ±0.5°C
Overheat protection: independent control circuit to protect against thermal runaway
Optional temperature program: 6 linear rates, 1, 2, 4, 8, 16, 32°C/min

Detector

Type: Sulfur or phosphorus flame photometric (FPD)
Temperature range: 100° to 400°C in 50° steps
Temperature regulation: Fully proportional, ±0.5°C
Overheat protection: fail-safe circuitry, line fuse
Accessory gas flow: ca. 150 cc/min prepurified H_2; ca. 40 cc/min prepurified air; ca. 10 cc/min prepurified O_2
Linear dynamic range: ca. 10^5 for phosphorus; 10^3 for sulfur (log)

Detector Amplifier

Type: Solid state two-stage, single channel
Sensitivity: 5×10^{-12} A full scale
Linear dynamic range: greater than 10^6 on all ranges
Drift: 4×10^{-14} A/hr @ constant ambient
Noise: 1×10^{-14} A with input capped
Background suppression: 0 to $\pm 10^{-8}$ A with coarse and fine adjustment
Attenuation: Input (range), X1, X10, X100, X1000, remote capability
Output (attenuator), X1, X2, X4, ...X1024
Outputs: for recorder, 1 mV; for integrator, 1 V; for computer, 10 V
Time constant: 1 sec maximum, less than 0.5 sec nominal

Requirements

Pressure regulated gas supplies: 0 to 100 psig N_2; 0 to 100 psig H_2; 0 to 100 psig O_2; 0 to 60 psig air, all gases, prepurified grade
Power: 117 V, 60 Hz (220 V, 50 Hz optional); 1800 W maximum
Size: 46.9 cm H, 56.2 cm W, 48.1 cm D (18-1/2" x 22-1/4" x 19")
Weight: 37 kg (85 lb)

References

a) Manufacturer's bulletin No. 5700 and supplement 5715
b) Manufacturer's catalog: Analytical Instruments for Chemistry, A 11-71

Features

Temperature programmer available

Cost

Gas chromatograph Model 5715A (option 005-011-017) $6,500.

Remarks

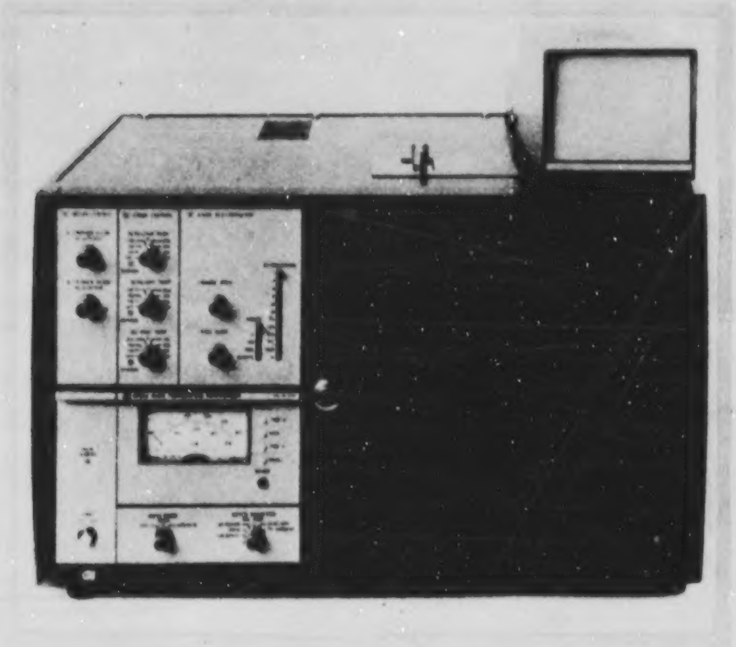
This model uses coiled GC columns only. Standard 2-m (6') glass U-tube columns can be used in the Hewlett-Packard 7610 series instruments (Hewlett-Packard 5)

Address

Hewlett-Packard
Analytical Instruments
Route 41
Avondale, PA 19311
(215) 268-2281 TWX 510-663-8268

Nitrogen/Phosphorus Analyzer

Gas Chromatograph Model 5714A (option-005-011-017)



Class	Laboratory: Routine analysis/research
Principle of Operation	Gas Chromatography - Thermionic Detection (GC-TID) for nitrogen and phosphorus
Sensitivity	10^{-12} g/sec nitrogen and phosphorus
Range	10^{-8} to 10^{-12} g/sec nitrogen and phosphorus
Interferences	Moderate interferences from iodinated hydrocarbons Slight or no interferences from hydrocarbons, including those containing Cl, Br, S
Multiparameter Capability	Convertible by manufacturer's representative to electron capture detection (ECD) for analysis of halogenated hydrocarbons (pesticides), flame photometric detection (FPD) for sulfur analysis; also flame ionization detection (FID) for oil analysis, thermal conductivity detection (TCD) for gas analysis (sewage digester gas).
Sampling	Method: Syringe injected aliquot of pesticide sample onto glass GC column
Sample Inlet	Type: Silicone rubber septa, screw-cap retained on stainless-steel injection ports, 1/8" or 1/4" sizes On-column injection: 1/8" and 1/4" sizes Glass Liners (inserts): 1/8" and 1/4" sizes Temperature range: 100° to 400°C in 50° steps Temperature regulation: Fully proportional, ±0.5°C Overheat protection: fail-safe circuitry, line fuse

Column Oven	Type: Dual columns and injection ports, glass or metal columns, vertically coiled; thermostatted, forced air circulation Carrier gas: N_2, prepurified Flow control: independent differential flow regulators; Flow range, tolerance: 2 to 200 cc/min He, ±0.3% Flow calibration: soap bubble flowmeter Column capacity: 1/8" O.D. glass tubing, 2 ea.: 30' 1/4" O.D. glass tubing, 2 ea.: 15' Temperature range: Continuously adjustable, ambient to 400°C Temperature regulation: Fully proportional, ±0.5°C Overheat protection: independent control circuit to protect against thermal runaway Optional temperature program: 6 linear rates, 1, 2, 4, 8, 16, 32°C/min
Detector	Type: Nitrogen/phosphorus selective thermionic (TID) Temperature range: 100° to 400° C in 50° steps Temperature regulation: Fully proportional, ±0.5°C Overheat protection: fail-safe circuitry, line fuse Accessory gas flow: ca. 30 cc/min prepurified H_2; ca. 180 cc/min prepurified air Linear dynamic range: Greater than 10^4
Detector Amplifier	Type: Solid state two-stage, single channel Sensitivity: 5×10^{-12} A full scale Linear dynamic range: greater than 10^6 on all ranges Drift: 4×10^{-14} A/hr @ constant ambient Noise: 1×10^{-14} A with input capped Background suppression: 0 to $\pm 10^{-6}$ A with coarse and fine adjustment Attenuation: Input (range), X1, X10, X100, X1000, remote capability Output (attenuator), X1, X2, X4, ...X1024 Outputs: for recorder, 1 mV; for integrator, 1 V; for computer, 10 V Time Constant: 1 sec maximum, less than 0.5 sec nominal
Requirements	Pressure regulated gas supplies: 0 to 100 psig He; 0 to 100 psig H_2; 0 to 60 psig air; all gases, prepurified grade Power: 117 V, 60 Hz (220 V, 50 Hz optional); 1800 W maximum Size: 46.9 cm H, 56.2 cm W, 48.1 cm D (18-1/2" x 22-1/4" x 19") Weight: 37 kg (85 lb)
References	a) Manufacturer's bulletin No. 5700 and supplement 5714 b) Manufacturer's catalog: Analytical Instruments for Chemistry, A 11-71
Features	
Cost	Gas chromatograph Model 5714 A (option 005-011-017) $4,160.
Remarks	This model uses coiled GC columns only. Standard 2-m (6') glass U-tube columns can be used in the Hewlett-Packard 7610 series instruments (Hewlett-Packard 6). Carrier gas should be He.
Address	Hewlett-Packard Analytical Instruments Route 41 Avondale, PA 19311 (215) 268-2281 TWX 510-663-8268

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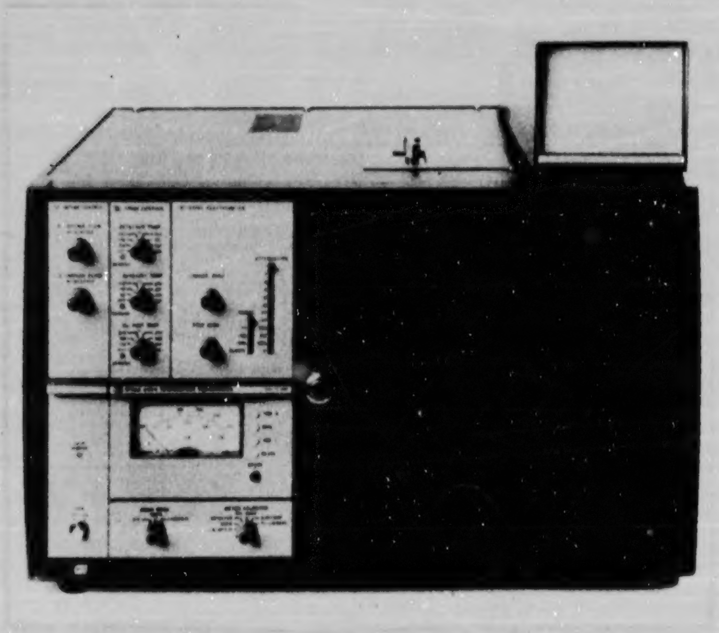
Halogenated Hydrocarbon Analyzer

Gas Chromatograph Model 5713A (option-055-011-017)



Class	Laboratory: Routine analysis/research
Principle of Operation	Gas Chromatography - Electron Capture Detection (GC-ECD)
Sensitivity	10^{-11} g lindane ($C_6H_6Cl_6$)
Range	10^{-7} to 10^{-11} g lindane
Interferences	Appreciable interferences from: other halogenated and conjugated unsaturated organic compounds in general, also nitro and cyano groups Moderate interferences from: oxygenated or nitrogenous organics, O_2, H_2O Slight or no interferences from: GC column and septum bleed, saturated hydrocarbons and fixed gases, among others
Multiparameter Capability	Convertible by manufacturer's representative to thermionic detection (TID) for analysis of nitrogen/phosphorus (pesticides), flame photometric detection (FPD) for sulfur/phosphorus analysis; also flame ionization detection (FID) for oil analysis, thermal conductivity detection (TCD) for gas analysis (sewage digester gas).
Sampling	Method: Syringe injected aliquot of pesticide sample onto glass GC column
Sample Inlet	Type: Silicone rubber septa, screw-cap retained on stainless-steel injection ports, 1/8" or 1/4" sizes On-column injection: 1/8" and 1/4" sizes Glass Liners (inserts): 1/8" and 1/4" sizes Temperature range: 100° to 400°C in 50° steps Temperature regulation: Fully proportional, ±0.5°C Overheat protection: fail-safe circuitry, line fuse

Column Oven	Type: Dual columns and injection ports; glass or metal columns, vertically coiled; thermostatted, forced air circulation Carrier gas: N_2, prepurified Flow control: independent differential flow regulators; Flow range, tolerance: 2 to 200 cc/min He, ±0.3% Flow calibration: soap bubble flowmeter Column capacity: 1/8" O.D. glass tubing, 2 ea.: 30' 1/4" O.D. glass tubing, 2 ea.: 15" Temperature range: Continuously adjustable, ambient to 400°C Temperature regulation: Fully proportional, ±0.5°C Overheat protection: independent control circuit to protect against thermal runaway Optional temperature program: 6 linear rates, 1, 2, 4, 8, 16, 32°C/min
Detector	Type: High temperature electron capture (ECD); 15 millicuries Ni^{63} Temperature range: 100° to 400°C in 50° steps Temperature regulation: Fully proportional, ±0.5°C Overheat protection: fail-safe circuitry; independent cutoff Pt sensor, 370°C Linear dynamic range: 10^4 for many compounds
Requirements	Pressure regulated gas supplies: 0 to 100 psig 5% methane in argon (carrier)
References	a) Manufacturer's bulletin No. 5700 and technical paper No. 49 b) Manufacturer's catalog: Analytical Instruments for Chemistry, A 11-71
Features	Wider dynamic range, linear electron capture detector (ECD)
Cost	Gas chromatograph Model 5713A (option 005-011-017) $3,985.
Remarks	This model uses coiled GC columns only. Standard 2-m (6') glass U-tube columns can be used in the 7610 series instruments (Hewlett-Packard 4)
Address	Hewlett-Packard Analytical Instruments Route 41 Avondale, PA 19311 (215) 268-2281 TWX 510-663-8268

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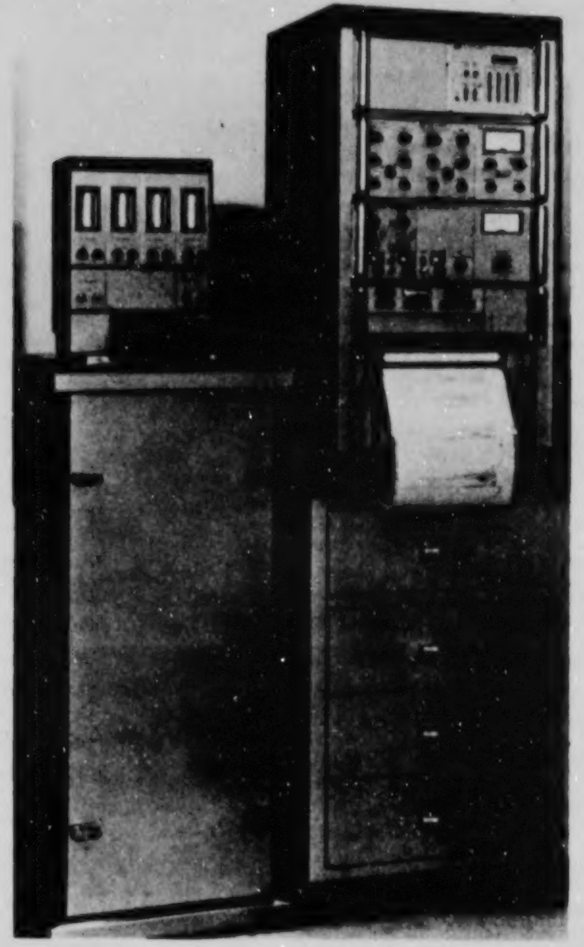
Halogenated Hydrocarbon Analyzer

Gas Chromatograph Model 7613A



Class	Laboratory: Routine analysis/research
Principle of Operation	Gas Chromatography - Electron Capture Detection (GC-ECD)
Sensitivity	10^{-10} g lindane ($C_6H_6Cl_6$)
Range	10^{-7} to 10^{-10} g lindane
Interferences	Appreciable interferences from: other halogenated and conjugated unsaturated organic compounds in general, also nitro and cyano groups Moderate interferences from: oxygenated or nitrogenous organics, O_2, H_2O Slight or no interferences from: GC column and septum bleed, saturated hydrocarbons and fixed gases, among others
Multiparameter Capability	Convertible by manufacturer's representative to electron capture detection (ECD) for analysis of halogenated hydrocarbons (pesticides) thermal conductivity detection (TCD) for gas analysis (sewage digester gas), flame photometric detection (FPD) for sulfur analysis

Sampling	Method: Syringe injected aliquot of pesticide sample onto glass GC column
Sample Inlet	Type: Silicone rubber septa, screw-cap retained on stainless-steel injection ports, 1/4" size On-column injection: in 1/4" size Glass Liners (inserts): Available in 1/4" size Temperature range: ambient to 400°C Temperature regulation: Fully proportional, ±0.5°C Overheat protection: fail-safe circuitry, line fuse
Column Oven	Type: Dual, 2-m (6') vertical glass U-tube GC columns and injection ports; thermostatted, forced air circulation Carrier gas: 5% methane in argon Flow control: independent differential flow regulators; Flow range, tolerance: 2 to 200 cc/min, ±0.3% Flow calibration: uncalibrated rotameters Column capacity: Standard, 1/4" O.D. glass tubing, 2 ea.: 6' Optional, 1/4" O.D. metal tubing, 2 ea.: 50' Temperature range: Continuously adjustable, ambient to 400°C Temperature regulation: Fully proportional, ±0.1°C Overheat protection: independent control circuit to protect against thermal runaway Optional temperature program: 10 linear rates, from 0.5 to 30 °C/min in 3 stages
Detector	Type: Electron Capture (ECD); 2 millicuries Ni^{63} Temperature range: ambient to 400°C Temperature regulation: Fully proportional, ±1°C Overheat protection: Accessory gas flow: none required Non-linear dynamic range: 10^3
Detector Amplifier	Type: Solid state two-stage, single channel Sensitivity: 1×10^{-12} A full scale Linear dynamic range: 10^6 Drift: $<10^{-14}$ A/hr @ constant ambient Noise: $<10^{-14}$ A with cables disconnected Background suppression: 0 to $\pm 10^{-10}$ A with coarse and fine adjustment Attenuation: Input (range), X1, X10, ...X10,000 Output (attenuator), X1, X2, X4, ...X256 Outputs: for recorder, 1 mV; for integrator, 1 V; for computer, 10 V Time Constant: 0.3 sec maximum
Requirements	Pressure regulated gas supplies: 0 to 60 psig 5% methane in argon Power: 117 V, 60 Hz (220 V, 50 Hz optional); 1800 W maximum Size: 166.4 cm H, 53.3 cm W, 53.3 cm D (64" x 21" x 21")-oven only (27-1/2" x 21" x 22")-electronics Weight: 166 kg (365 lb) total
References	a) Manufacturer's bulletin No. 7610 b) Manufacturer's catalog: Analytical Instruments for Chemistry, A 11-71
Features	The flame ionization version, Model 7611A ($6,405.) can be converted to nitrogen/phosphorus thermionic detection (see Hewlett-Packard 2)
Cost	Gas chromatograph Model 7613A $6,595.
Remarks	This vertical U-tube column oven accomodates 2 standard 2-m (6') glass columns and has room for 2 more columns
Address	Hewlett-Packard Analytical Instruments Route 41 Avondale, PA 19311 (215) 268-2281 TWX 510-663-8268

INSTRUMENTATION
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Halogenated Hydrocarbon Analyzer

Gas Chromatograph Model 417 (8044)

Packard
MODEL 417

Class	Laboratory: Routine analysis/research
Principle of Operation	Gas Chromatograph - Electron Capture Detection (GC-ECD)
Sensitivity	10^{-11} g lindane ($C_6H_6Cl_6$)
Range	10^{-8} to 10^{-11} g lindane
Interferences	Appreciable interferences from: other halogenated and conjugated unsaturated organic compounds in general, also nitro and cyano groups Moderate interferences from: oxygenated or nitrogenous organics, O_2, H_2O Slight or no interferences from: GC column and septum bleed, saturated hydrocarbons and fixed gases, among others
Multiparameter Capability	Convertible by manufacturer's representative to : thermionic detection (TID) for analysis of organic phosphates (pesticides), thermal conductivity detection (TCD) for gas analysis (sewage digester gas), flame photometric detection (FPD) for sulfur analysis, flame ionization detection (FID) for oil analysis
Sampling	Method: Syringe injected aliquot of pesticide sample onto glass GC column

Sample Inlet	Type: Silicone rubber septa, screw-cap retained on 1/8" and 1/4" standard stainless-steel injection ports On-column injection: Standard for 6 mm glass column Glass liners (inserts): Available in 1/4" size, adaptable to 1/8" Temperature range: 70° to 500°C Temperature regulation: Fully proportional, ±0.05°C at 150°C Overheat protection: Optional variable bimetallic temperature limit switch
Column Oven	Type: Dual columns, injection ports and detectors; glass or metal columns, vertically coiled; thermostatted, forced air circulation Carrier gas: N_2 or 5% methane in argon Flow control: independent differential flow regulators Flow range, tolerance: 2 to 100 cc/min He, ±0.1% Flow calibration: soap bubble flowmeter Column capacity: Standard, 1/4" O.D. glass tubing, 2 ea.: 10' Optional, 1/4" O.D. metal tubing, 2 ea.: 30' Temperature range: continuously adjustable, ambient to 500°C Temperature regulation: fully proportional, ±0.2°C Overheat protection: optional variable bimetallic temperature limit switch Optional temperature program: 80 linear rates, 0.1 to 3.9° in 0.1° steps, 1 to 39° in 1° steps
Detector	Type: High temperature electron capture (ECD), 15 millicuries Ni^{63} Temperature range: Ambient to 500°C Temperature regulation: Fully proportional, ±0.1°C Overheat protection: Optional variable bimetallic temperature limit switch Accessory gas flow: ca. 40 cc/min 5% methane in argon Linear dynamic range: 10^5
Detector Amplifier	Type: Solid state, electrometer tube, single channel Sensitivity: 2.5×10^{-12} A full scale Linear dynamic range: 2×10^7 overall Drift: Less than 1%/hr at constant ambient Noise: 2.5×10^{-14} A with cable Background suppression: 0 to $\pm 5 \times 10^{-10}$ A with coarse and fine adjustment Attenuation: Input (range), X1, X10, X100 Output (attenuator), X1, X2, X4, ...X2048 Outputs: for 1, 2.5 mV; for integrator and computer 1V Time constant: 0.2 sec maximum
Requirements	Recorder: 1 mV, servo-type, strip chart Pressure regulated gas supplies: 0 to 100 psig N_2 or 5% methane in argon, all gases, prepurified grade Power: 117 V, 60 Hz (220 V, 50 Hz optional); 2500 W maximum Size: 55.9 cm H, 75 cm W, 45 cm D (22" x 29.5" x 17.1") Weight: 70 kg (154 lb)
Reference	Manufacturer's brochure No. 1191
Features	Includes pulse power supply for ECD. Digital linear temperature programmer (option 23) with automatic cooling available ($1,065. additional).
Cost	Gas chromatograph model 8044 $3,825.
Remarks	Model 8065-Ni ($6,930.) has vertical U-tube oven for 2 ea. 4-1/2' (1.5-m) glass U-tube columns.
Address	Packard Instrument Co. 2200 Warrenville Rd. Downers Grove, IL 60515 (312) 969-6000 Telex 72-8378 TWX 910/695-3220

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

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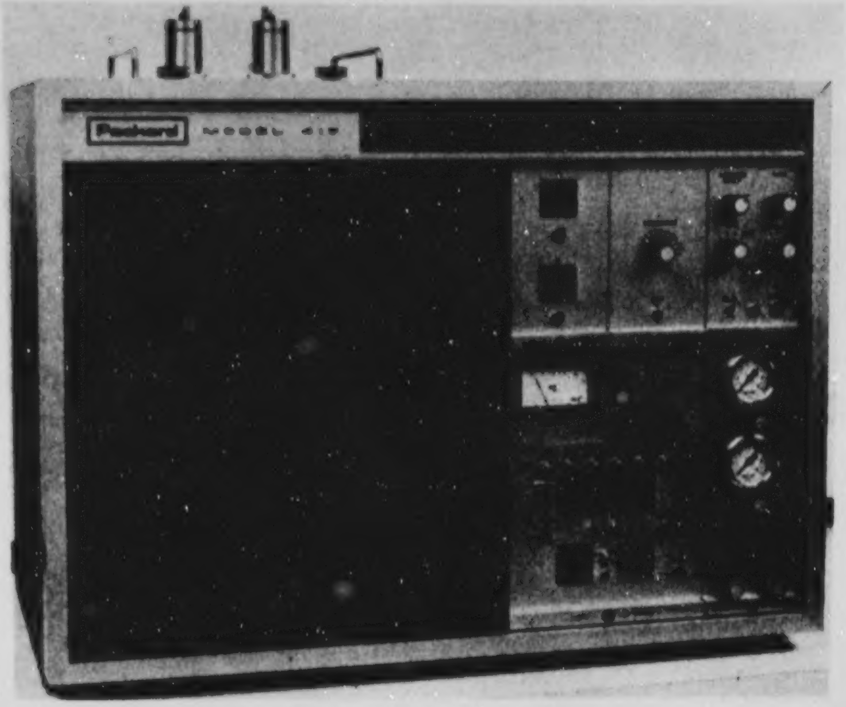
Phosphorus/Nitrogen Analyzer

Gas Chromatograph Model 417 (8045/8046)



Class	Laboratory: Routine analysis/research
Principle of Operation	Gas Chromatograph - Thermionic Detection (GC-TID)
Sensitivity	10^{-12} g/sec
Range	10^{-} to 10^{-12} g/sec
Interferences	
Multiparameter Capability	Convertible by manufacturer's representative to: electron capture detection (ECD) for analysis of halogenated hydrocarbons (pesticides), flame photometric detection (FPD) for sulfur analysis, flame ionization detection for oil analysis, thermal conductivity detection (TCD) for gas analysis (sewage digester gas).
Sampling	Method: Syringe injected aliquot of pesticide sample onto glass GC column
Sample Inlet	Type: Silicone rubber septa, screw-cap retained on 1/8" and 1/4" standard stainless-steel injection parts On-column injection: Standard for 6 mm glass column Glass liners (inserts): Available in 1/4" size, adaptable to 1/8" Temperature range: 70° to 500°C Temperature regulation: Fully proportional, ±0.05°C at 150°C Overheat protection: Optional variable bimetallic temperature limit switch

Column Oven	Type: Dual columns, injection ports and detectors; glass or metal columns, vertically coiled; thermostatted, forced air circulation Carrier gas: N_2 or 5% methane in argon Flow control: independent differential flow regulators Flow range, tolerance: 2 to 100 cc/min He, ±0.1% Flow calibration: soap bubble flowmeter Column capacity: Standard, 1/4" O.D. glass tubing, 2 ea.: 10' Optional, 1/4" O.D. metal tubing, 2 ea.: 30' Temperature range: continuously adjustable, ambient to 500°C Temperature regulation: fully proportional, ±0.2°C Overheat protection: optional variable bimetallic temperature limit switch Optional temperature program: 80 linear rates, 0.1 to 3.9" in 0.1° steps, 1 to 39° in 1° steps
Detector	Type: Thermionic (TID) for phosphorus/nitrogen Temperature range: ambient to 500°C Temperature regulation: Fully proportional, ±0.1°C Overheat protection: optional variable bimetallic temperature limit switch Accessory gas flow: ca. 30 cc/min prepurified H_2; ca. 300 cc/min prepurified air per FID Linear dynamic range: 10^6
Detector Amplifier	Type: Solid state, electrometer tube, single channel Sensitivity: 2.5×10^{-12} A full scale Linear dynamic range: 2×10^7 overall Drift: Less than 1%/hr at constant ambient Noise: 2.5×10^{-14} A with cable Background suppression: 0 to $\pm 5 \times 10^{-10}$ A with coarse and fine adjustment Attenuation: Input (range), X1, X10, X100 Output (attenuator), X1, X2, X4, ...X2048 Outputs: for 1, 2.5 mV; for integrator and computer 1V Time constant: 0.2 sec maximum
Requirements	Pressure regulated gas supplies: 0 to 100 psig He; 0 to 100 psig H_2; 0 to 100 psig air; all gases, prepurified grade
Reference	Manufacturer's brochure No. 1191
Features	
Cost	Gas chromatograph model 8045/8046 $2,670.
Remarks	
Address	Packard Instrument Co. 2200 Warrenville Rd. Downers Grove, IL 60515 (312) 969-6000 Telex 72-8378 TWX 910/695-3220

805

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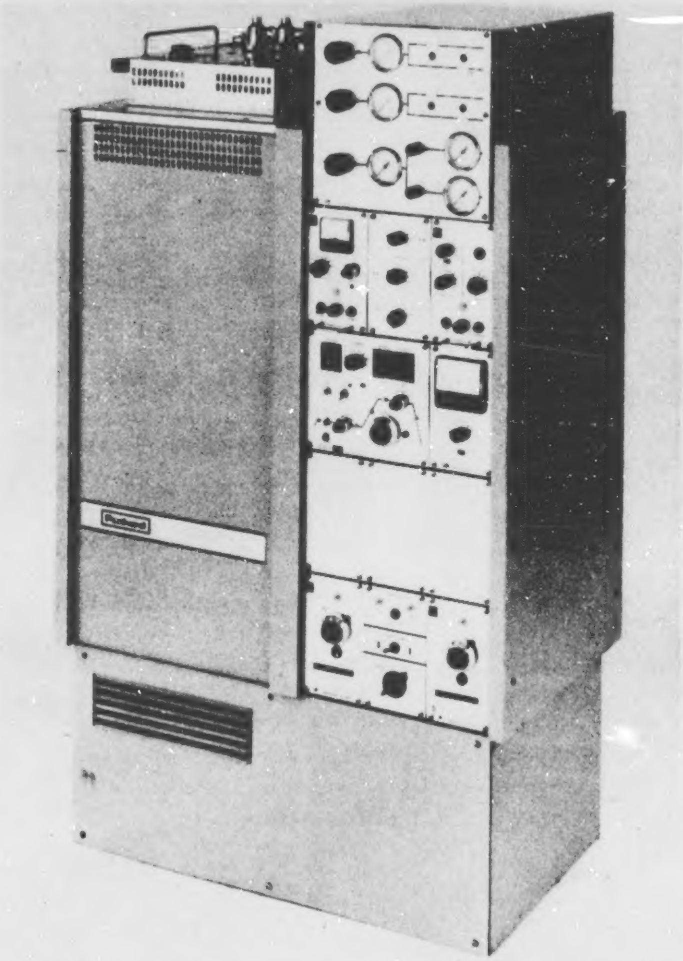
Halogenated Hydrocarbon Analyzer

Gas Chromatograph Series 420, Model 8061-25(Ni)

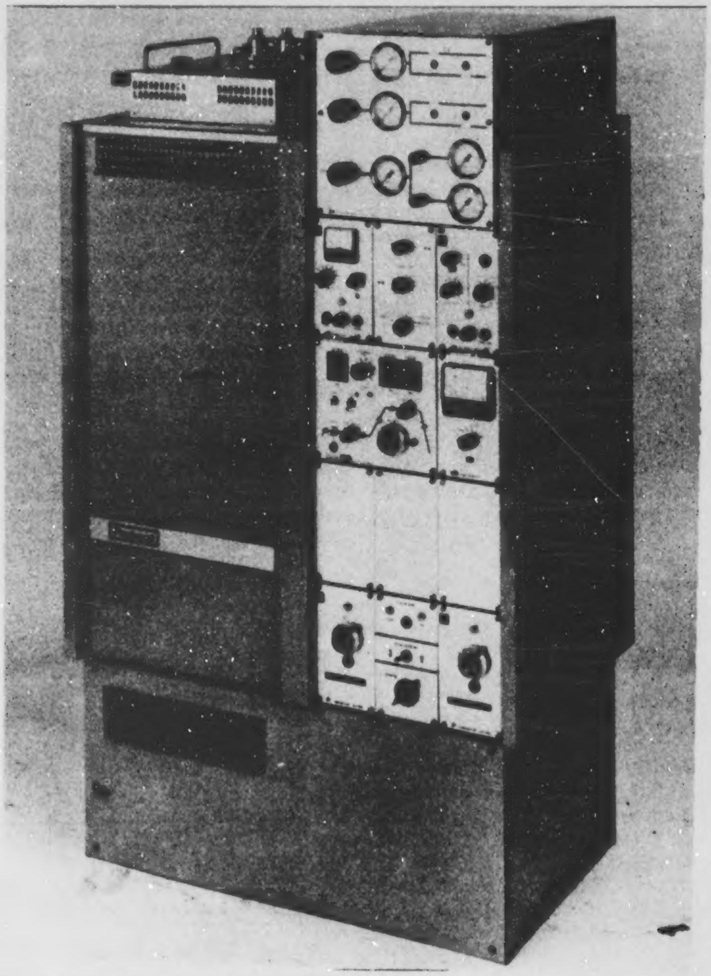


Class	Laboratory: Routine analysis/research
Principle of Operation	Gas Chromatograph - Electron Capture Detection (GC-ECD)
Sensitivity	10^{-11} g lindane
Range	10^{-8} to 10^{-11} g lindane
Interferences	Appreciable interferences from: other halogenated and conjugated unsaturated organic compounds in general, also nitro and cyano groups Moderate interferences from: oxygenated or nitrogenous organics, O_2, H_2O Slight or no interferences from: GC column and septum bleed, saturated hydrocarbons and fixed gases, among others
Multiparameter Capability	Convertible by manufacturer's representative to: thermionic detection (TID) for analysis of organic phosphates (pesticides), thermal conductivity detection (TCD) for gas analysis (sewage digester gas), flame photometric detection (FPD) for sulfur analysis, flame ionization detection (FID) for oil analysis
Sampling	Method: Syringe injected aliquot of pesticide sample onto glass GC column

Sample Inlet	Type: Silicone rubber septa, screw-cap retained on 1/8" and 1/4" standard stainless-steel injection parts On-column injection: Standard for 6 mm glass column Glass liners (inserts): Available in 1/4" size, adaptable to 1/8" Temperature range: 70° to 500°C Temperature regulation: Fully proportional, ±0.05°C at 150°C Overheat protection: Optional variable bimetallic temperature limit switch
Column Oven	Type: Dual 4-1/2" (1.5m) glass (6mm O.D.) vertical U-tubes; thermostatted, forced air circulation Carrier gas: N_2 or 5% methane in argon Flow control: independent differential flow regulators Flow range, tolerance: 2 to 100 cc/min He, ±0.1% Flow calibration: soap bubble flowmeter Column capacity: Standard, 1/4" O.D. glass tubing, 2 ea.: ' Optional, 1/4" O.D. metal tubing, 2 ea.: 30' Temperature range: continuously adjustable, ambient to 500°C Temperature regulation: Fully proportional, ±0.2°C Overheat protection: optional variable bimetallic temperature limit switch Optional temperature program: 80 linear rates, 0.1 to 3.9° in 0.1° steps, 1° to 39° in 1° steps
Detector	Type: High temperature electron capture (ECD), 15 millicuries Ni^{63} Temperature range: Ambient to 500°C Temperature regulation: Fully proportional, ±0.1°C Overheat protection: Optional variable bimetallic temperature limit switch Accessory gas flow: ca. 40 cc/min 5% methane in argon Linear dynamic range: 10^3
Detector Amplifier	Type: Solid state, electrometer tube, single channel Sensitivity: 2.5×10^{-12} A full scale Linear dynamic range: 2×10^7 overall Drift: Less than 1%/hr at constant ambient Noise: 2.5×10^{-14} A with cable Background suppression: 0 to $\pm 5 \times 10^{-10}$ A with coarse and fine adjustment Attenuation: Input (range), X1, X10, X100 Output (attenuator), X1, X2, X4, ...X2048 Outputs: for 1, 2.5 mV; for integrator and computer 1V Time constant: 0.2 sec maximum
Requirements	Power: 117 V, 60 Hz (220 V, 50 Hz optional); 2500 W maximum Size: 140 cm H, 78 cm W, 42 cm D (55" x 30" x 16.5") Weight: 90 kg (200 lb)
Reference	Manufacturer's brochure No. 1124A
Features	
Cost	Gas chromatograph model 8061-25(Ni) $5,830.
Remarks	
Address	Packard Instrument Co. 2200 Warrenville Rd. Downers Grove, IL 60515 (312) 969-6000 Telex 72-8378 TWX 910/695-3220

Phosphorus/Nitrogen Analyzer

Gas Chromatograph Series 420, Model 8061-24



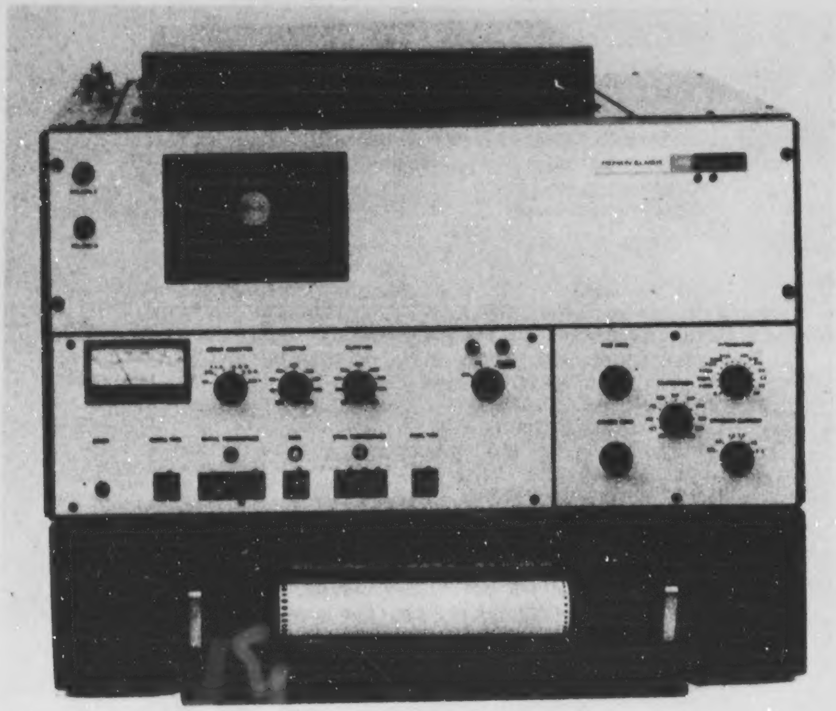
Class	Laboratory: Routine analysis/research
Principle of Operation	Gas Chromatograph - Thermionic Detection (GC-TID)
Sensitivity	10^{-12} g/sec
Range	10^{-} to 10^{-12} g/sec
Interferences	
Multiparameter Capability	Convertible by manufacturer's representative to: electron capture detection (ECD) for analysis of halogenated hydrocarbons (pesticides), flame photometric detection (FPD) for sulfur analysis, flame ionization detection for oil analysis, thermal conductivity detection (TCD) for gas analysis (sewage digester gas).
Sampling	Method: Syringe injected aliquot of pesticide sample onto glass GC column

Sample Inlet	Type: Silicone rubber septa, screw-cap retained on 1/8" and 1/4" standard stainless-steel injection parts On-column injection: Standard for 6 mm glass column Glass liners (inserts): Available in 1/4" size, adaptable to 1/8" Temperature range: 70° to 500°C Temperature regulation: Fully proportional, ±0.05°C at 150°C Overheat protection: Optional variable bimetallic temperature limit switch
Column Oven	Type: Dual 4-1/2" (1.5 m) glass (6mm O.D.) vertical U-tubes; thermostatted, forced air circulation Carrier gas: N_2 or 5% methane in argon Flow control: independent differential flow regulators Flow range, tolerance: 2 to 100 cc/min He, ±0.1% Flow calibration: soap bubble flowmeter Column capacity: Standard, 1/4" O.D. glass tubing, 2 ea.: 10' Optional, 1/4" O.D. metal tubing, 2 ea." 30' Temperature range: continuously adjustable, ambient to 500°C Temperature regulation: Fully proportional, ±0.2°C Overheat protection: optional variable bimetallic temperature limit switch Optional temperature program: 80 linear rates, 0.1 to 3.9° in 0.1° steps, 1° to 39° in 1° steps
Detector	Type: Thermionic (TID) for phosphorus/nitrogen Temperature range: ambient to 500°C Temperature regulation: Fully proportional, ±0.1°C Overheat protection: optional variable bimetallic temperature limit switch Accessory gas flow: *ca.* 30 cc/min prepurified H_2; *ca.* 300 cc/min prepurified air per FID Linear dynamic range: 10^6
Detector Amplifier	Type: Solid state, electrometer tube, single channel Sensitivity: 2.5×10^{-12} A full scale Linear dynamic range: 2×10^7 overall Drift: Less than 1%/hr at constant ambient Noise: 2.5×10^{-14} A with cable Background suppression: 0 to $\pm 5 \times 10^{-10}$ A with coarse and fine adjustment Attenuation: Input (range), X1, X10, X100 Output (attenuator), X1, X2, X4, ...X2048 Outputs: for 1, 2.5 mV; for integrator and computer 1V Time constant: 0.2 sec maximum
Requirements	Recorder: 1 mV, servo-type, strip chart Pressure regulated gas supplies: 0 to 100 psig He; 0 to 100 psig H_2; 0 to 100 psig air; all gases, prepurified grade Power: 117 V, 60 Hz (220 V, 50 Hz optional); 2500 W maximum Size: 140 cm H, 78 cm W, 42 cm D (55" x 30" x 16.5") Weight: 90 kg (200 lb)
Reference	Manufacturer's brochure No. 1191
Features	
Cost	Gas chromatograph model 8061-24 $
Remarks	
Address	Packard Instrument Co. 2200 Warrenville Rd. Downers Grove, IL 60515 (312) 969-6000 Telex 72-8378 TWX 910/695-3220

H2O-PES
Pesticide Analysis
Perkin-Elmer 1
October, 1973

Halogenated Hydrocarbon Analyzer

Gas Chromatograph Model 3920 (Option 045-0006)



Class	Laboratory: routine analysis/research
Principle of Operation	Gas Chromatography - Electron Capture Detection (GC-ECD)
Sensitivity	10^{-12} g lindane ($C_6H_6Cl_6$)
Range	10^{-8} to 10^{-12} g lindane
Interferences	Appreciable interferences from: other halogenated and conjugated unsaturated organic compounds in general, also nitro and cyano groups Moderate interferences from: oxygenated or nitrogenous organics, O_2, H_2O Slight or no interferences from: GC column and septum bleed, saturated hydrocarbons and fixed gases, among others
Multiparameter Capability	Convertible by manufacturer's representative to dual ECD for simultaneous dual column analysis of halogenated compounds, flame photometric detection (FPD) for phosphorus or sulfur containing pesticides, thermionic (alkali-flame) detection (TID) for selective response to phosphorus compounds (oranophosohorus pesticides), flame ionization detection (FID) for oil analysis, conductivity detection (TCD) for gas analysis (sewage digester gas).
Sampling	Method: Syringe injected aliquot of pesticide sample onto glass GC column
Sample Inlet	Type: Silicone rubber septa, screw-cap retained on interchangable stainless-steel injection ports, 1/8" or 1/4" sizes On-column injection: 1/8" and 1/4" sizes Optional heated injector with glass liners (inserts): Available in 1/8" and ¼" sizes Temperature range: Continuously adjustable, 50° to 400°C Temperature regulation: Fully proportional, ±1% Overheat protection: Diode overcurrent limiting protector

Column Oven

Type: Dual columns, injection ports and detectors; glass or metal columns, horizontally coiled; thermostatted, forced air circulation
Carrier gas: 5% methane in argon
  Optional flow control: independent differential flow controllers
  Flow range, tolerance: 2 to 200 cc/min He, ±0.3%
  Flow calibration: soap bubble flowmeter
Column capacity:
  Standard, 1/8" O.D. metal tubing, 2 ea.: 52'
  Optional, 1/4" O.D. metal tubing, 2 ea.: 24'
Temperature range: Continuously adjustable, ambient to 400°C at 1° intervals
Temperature regulation: Fully proportional, ±0.5°C
Overheat protection: Cut-off circuitry adjusted for 30°C above set-point
Optional Temperature program: 7 linear rates, 0.5, 1, 2, 4, 8, 16, 32°C/min

Detector and Amplifier

Type: High temperature electron capture (ECD), 10.5 millicuries Ni^{63}
Temperature range: Continuously adjustable 100° to 350°C
Temperature regulation: Fully proportional, ±1°C
Overheat protection: Diode overcurrent limiting protector at 370°C
Accessory gas flow: none required
Linear dynamic range: 10^4
Electronics: Solid state design, single channel
Standing current: 0.5, 1.0, 2.0, 3.0 and 3.5×10^{-9}A
Pulse voltage: -55V
Pulse width: 0.25 μ sec
System noise: 10 μ V at recorder; 2 Hz at 3×10^{-9}A standing current
Amplifier noise: 0.2 Hz
Attenuation: Output X1, X2, X4,...X4096
Outputs: For recorder, 1 mV; for electronic integrators 1V; for computer 9 V
Time constant: 0.38 sec

Requirements

Recorder: 1 mV, servo type, strip chart
Pressure regulated gas supplies: 0 to 100 psig 5% methane in argon prepurified grade
Power: 117 V, 60 Hz (220 V, 50 Hz optional); 2200 maximum
Size: 45.7 cm H, 72.2 cm W, 55.9 cm D (18" x 28" x 22")
Weight: kg (lb)

Features

References

Manufacturer's bulletin No. L-160 and PL 154

Cost

Gas chromatograph model 3920 (045-0006) $3,550.

Remarks

Option 045-0934 ($1,200.) adds a second Ni^{63} ECD and amplifier channel for simultaneous dual independent ECD operation

Address

Perkin-Elmer Corporation
Instrument Division
Norwalk, CT 06852
(203) 762-4811
Cable PECO-NORWALK

H2O-PES
Pesticide Analysis
Perkin-Elmer 2
October 1973

Halogen/Phosphorus Analyzer (Thermionic)

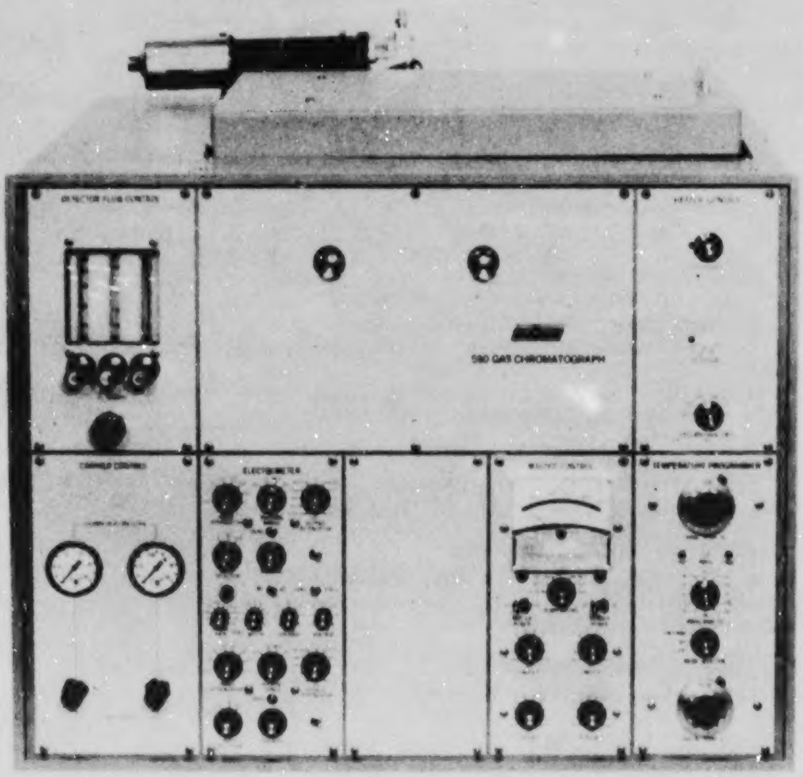
Gas Chromatograph Model 3920 (Option 045-0004-0096)

Class	Laboratory: routine analysis/research
Principle of Operation	Gas Chromatography - Flame Ionization/Thermionic Detection (GC-FID/TID)
Sensitivity	10^{-10} g phosphorus; 10^{-8} g lindane ($C_6H_6Cl_6$)
Range	10^3:1
Interferences	Slight interference from organics 10,000:1
Multiparameter Capability	Convertible by manufacturer's representative to electron capture detection (ECD) for analysis of halogenated hydrocarbons (pesticides), thermal conductivity detection(TCD) for gas analysis (sewage digester gas).
Sampling	Method: Syringe injected aliquot of pesticide sample onto glass GC column
Sample Inlet	Type: Silicone rubber septa, screw-cap retained on interchangable stainless-steel injection ports, 1/8" or 1/4" sizes On-column injection: 1/8" and 1/4" sizes Optional heated injector with glass liners (inserts): available in 1/8" and 1/4" sizes Temperature range: Continuously adjustable, 50° to 400°C Temperature regulation: Fully proportional, ±1% Overheat protection: Diode overcurrent limiting protector

Column Oven	Type: Dual columns, injection ports and detectors; glass or metal columns, horizontally coiled; thermostatted, forced air circulation Carrier gas: Helium or nitrogen Optional Flow control: independent differential flow controllers Flow range, tolerance: 2 to 200 cc/min He, ±0.3% Flow calibration: soap bubble flowmeter Column capacity: Standard, 1/8" O.D. metal tubing, 2 ea.: 52' Optional, 1/4" O.D. metal tubing, 2 ea.: 24' Temperature range: Continuously adjustable, ambient to 400°C at 1° intervals Temperature regulation: Fully proportional, ±0.5°C Overheat protection: Cut-off circuitry adjusted for 30°C above set-point Optional temperature program: 7 linear rates, 0.5, 1, 2, 4, 8, 16, 32°C/min
Detector	Type: Independent or compensating dual flame ionization (FID) with single thermionic (alkali flame) capability Temperature range: Continuously adjustable, 50° to 400°C Temperature regulation: Fully proportional, ±1°C Overheat protection: Diode overcurrent limiting protector Accessory gas flow: ca. 40 cc/min prepurified H_2; ca. 600 cc/min prepurified air Linear dynamic range: greater than 10^6 (FID), greater than 10^3 (TID)
Detector Amplifier	Type: Solid state design, single or differential input Sensitivity: 5×10^{-12} A full scale Linear dynamic range: 10^5 on X1 input attenuation, 10^6 on all others Drift: Less than 3×10^{-14} A/wk at constant ambient temperature and line voltage Noise: 3×10^{-14} A, with detector cable Background suppression: 0 to $\pm 2 \times 10^{-8}$ A with coarse and fine adjustment Attenuation: Input (range), X1, X10, X100, X1000 Output (attenuator), X1, X2, X4, ...X1024 Outputs: For recorders, 1, 2.5, 5 mV; for electronic integrators 1V; for computer 10 V Time constant: 0.15 sec maximum, 0.03 sec nominal
Requirements	Pressure regulated gas supplies: 0 to 100 psig He; 0 to 100 psig H_2; 0 to 100 psig air; all gases prepurified grade Recorder: 1 mV, servo type, strip chart Power: 117 V, 60 Hz (220 V, 50 Hz optional); 2200 maximum Size: 45.7 cm H, 72.2 cm W, 55.9 cm D (18" x 28" x 22") Weight: kg (lb)
Features	Convertible to ECD; temperature programming available as option
References	a) Manufacturer's bulletin No. L-160 and price list No. PL-151
Cost	Gas chromatograph model 3920 (045-0004) $3,335. With TID accessory (045-0096)
Remarks	Accessory Amplifier (045-0168) provides independent, simultaneous operation of FID and TID $ 850
Address	Perkin-Elmer Corporation Instrument Division Norwalk, CT 06852 (203) 762-4811 Cable PECO-NORWALK

Halogenated Hydrocarbon Analyzer

Gas Chromatograph Series 550-ECD (Option 4201-1400-3201)

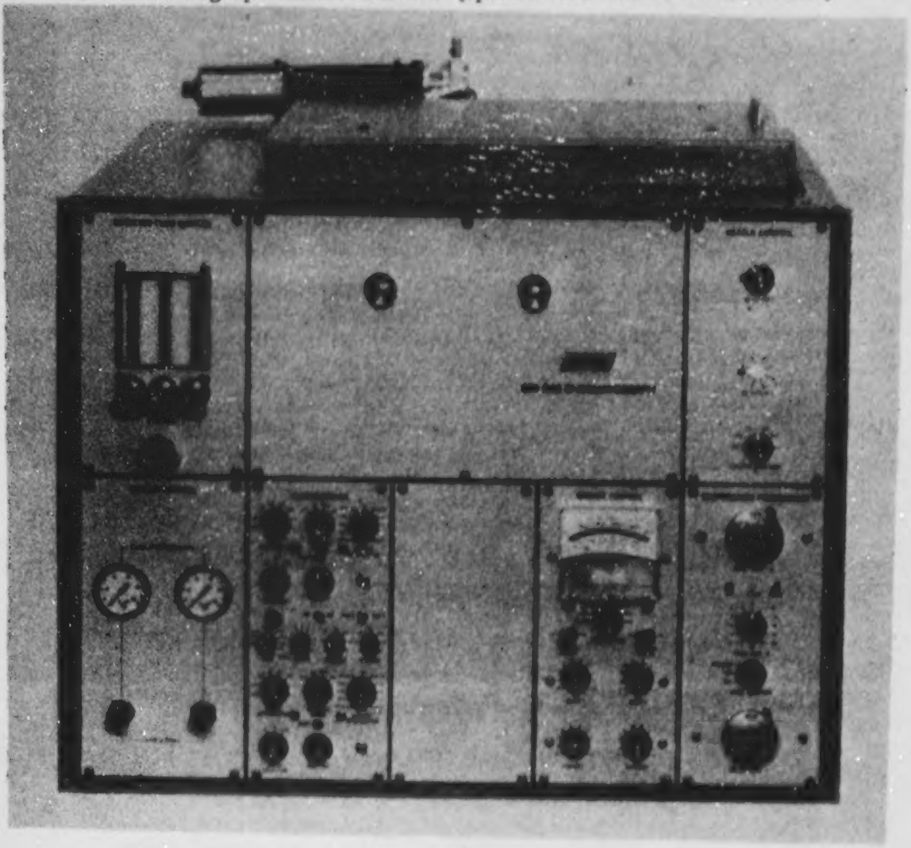


Class	Laboratory: routine analysis/research
Principle of Operation	Gas Chromatography - Electron Capture Detection (GC-ECD)
Sensitivity	10^{-12} g lindane ($C_6H_6Cl_6$)
Range	10^{-9} to 10^{-12} g lindane
Interferences	Appreciable interferences from: other halogenated and conjugated unsaturated organic compounds in general, also nitro and cyano groups Moderate interferences from: oxygenated or nitrogenous organics, O_2, H_2O GC column and septum bleed Slight or no interferences from: saturated hydro-carbons and fixed gases, among others.
Multiparameter Capability	Convertible by manufacturer's representative to: flame photometric detector (FPD) for phosphorus or sulfur analysis (pesticides), Coulson conductivity detector (CCD) specific for analysis of halogen, nitrogen or sulfur (pesticides), flame ionization detection (FID) for oil analysis, thermal conductivity detection (TCD) for gas analysis (sewage digester gas).
Sampling	Method: Syringe injected aliquot of pesticide sample onto glass GC column

Sample Inlet	Type: Silicone rubber septa, screw-cap retained on glass or stainless-steel injection ports On-column injection: 1/4" standard, also available in 1/16" and 1/8" sizes Glass liners (inserts): Available in 1/8" and 1/4" size Temperature range: Ambient to 450°C Temperature regulation: Solid state, thermocouple feedback Overheat protection: Line fuse only
Column Oven	Type: Dual columns and injection ports, glass or metal columns, vertically coiled; thermostatted, forced air circulation Carrier gas: 5% methane in argon or N_2 Flow control: independent differential flow regulators Flow range, tolerance: 2 to 200 cc/min He, ±0.3% Flow calibration: soap bubble flow meter and rotameters, standard Column capacity: Standard, 1/4" O.D. glass tubing, 2 ea.: 6' Optional, 1/4" O.D. metal tubing, 2 ea.: 20' Temperature range: Continuously adjustable, ambient to 400°C Temperature regulation: Fully proportional, ±0.25°C Overheat protection: Adjustable limit switch Optional temperature program: 49 linear rates, 1 to 50°/C in 1° steps
Detector	Type: High temperature electron capture (ECD), 15 millicuries Ni^{63} Temperature range: Ambient to 400°C Temperature regulation: Variac Overheat protection: Line fuse only Accessory gas flow: none required Linear dynamic range: Greater than 10^{4}
Detector Amplifier	Type: Pulsed frequency Sensitivity: 1×10^{-12} A full scale Linear dynamic range: 10^{4} Drift: Noise: Background suppression: Attenuation: Output (attenuator), X1, X2, X4, ...X4096 Outputs: For recorder, 1 mV; for computer 1 V Time constant: 0.3 sec maximum
Requirements	Recorder: 1 mV, servo-type, strip chart Pressure regulated gas supplies: 0 to 100 psig 5% methane in argon or N_2, prepurified grade Power: 117 V, 60 Hz (220 V, 50 Hz optional) Size: 50.8 cm H, 60.2 cm W, 60.2 cm D (20" x 24" x 24") Weight: 40.9 kg (90 lb)
Features	Includes new linear ECD. Optional automatic sampler available.
Cost	Gas Chromatograph Model 550 (Option 4201-1400-3201) $3,540.
Remarks	Option 4201-1400-3201-3201) ($5,135.) has standard independent, dual, high-temperature ECD capability
Address	Tracor Analytical Instruments 6500 Tracor Lane Austin, TX 78721 (512) 926-2800 TWX 910-874-1372 Cable TRACOR

Phosphorus/Sulfur Analyzer (FPD)

Gas Chromatograph Series 550-FPD (Option 4201-1400-3400-2100-5104)



Class	Laboratory: routine analysis/research
Principle of Operation	Gas Chromatography - Flame Photometric Detection (GC-FPD)
Sensitivity	10^{-11} g phosphorus or sulfur
Range	10^{-6} to 10^{-11} g for phosphorus; 10^{-8} to 10^{-11} g for sulfur
Interferences	Slight interferences (0.01%) from organic compounds
Multiparameter Capability	Convertible by manufacturer's representative to: electron capture detection (ECD) for analysis of halogenated hydrocarbons (pesticides), Coulson conductivity detector (CCD) specific for analysis of halogen, nitrogen or sulfur, flame ionization detector (FID) for oil analysis, thermal conductivity detection (TCD) for gas analysis (sewage digester gas).
Sampling	Method: Syringe injected aliquot of pesticide sample onto glass GC column

Sample Inlet

Type: Silicone rubber septa, screw-cap retained on glass or stainless-steel injection ports
On-column injection: Available in 1/16", 1/8" and 1/4" sizes
Glass liners (inserts): Available in 1/8" and 1/4" size
Temperature range: Ambient to 450°C
Temperature regulation: Solid state, thermocouple feedback
Overheat protection: Line fuse only

Column Oven

Type: Dual columns, injection parts and detectors; metal or glass columns, vertically coiled; thermostatted, forced air circulation
Carrier gas: He or N_2, prepurified
  Flow control: independent differential flow regulators
  Flow range, tolerance: 2 to 200 cc/min He, ±0.3%
  Flow calibration: soap bubble flow meter and rotameters, standard optional
Column capacity: Standard, 1/8" O.D. metal tubing, 2 ea.: 50'
                 Optional, 1/4" O.D. metal tubing, 2 ea.: 20'
Temperature range: Continuously adjustable, ambient to 400°C
Temperature regulation: Fully proportional ±0.25°C
Overheat protection: Adjustable limit switch
Optional temperature program: 49 linear rates, 1 to 50°/C in 1° steps
  Phosphorus or sulfur flame photometric detection (FPD)

Detector

Type: Independent or compensating dual flame ionization (FID)
Temperature range: Ambient to 250°C
Temperature regulation: Variac
Overheat protection: Line fuse only
Accessory gas flow: ca. 200 cc/min H_2; ca. 40 cc/min air; ca. 20 cc/min O_2; all gases prepurified
Linear dynamic range: Greater than 10^6

Detector Amplifier

Type: Solid state, parametric design, dual channel
Sensitivity: 1×10^{-12} A full scale
Linear dynamic range: 10^6
Drift: 1%/day at constant ambient
Noise: 1×10^{-14} A
Background suppression: Three ranges, 0 to $\pm 10^{-6}$, 10^{-8}, 10^{-10} A with coarse and fine adjustment
Attenuation: Input (range), X1, X10, X100, ...X1,000,000
             Output (attenuator), X1, X2, X4, ...X1024
Outputs: For recorder, 1 mV; for computer 1 V
Time Constant: 0.3 sec maximum

Requirements

Recorder: 1 mV, servo-type, strip chart
Pressure regulated gas supplies: 0 to 100 psig He; 0 to 100 psig H_2; 0 to 100 psig air; 0 to 30 psig O_2; all gases, prepurified grade
Power: 117 V, 60 Hz (200 V, 50 Hz optional)
Size: 50.8 cm H, 60.2 cm W, 60.2 cm D (20" x 24" x 24")
Weight: 40.9 kg (90 lb)

Reference

Manufacturer's 550 series brochure AB123 and price list APL-114

Features

Interchangeable light filters permit facile interconversion between phosphorus and sulfur detection; simultaneous FID operation with FPD

Cost

Gas Chromatograph Model 550 (Option 4201-1400-3400-2100-5104) $4,820.
plus 113640-0001 photomultiplier dynode power supply $5,145.

Remarks

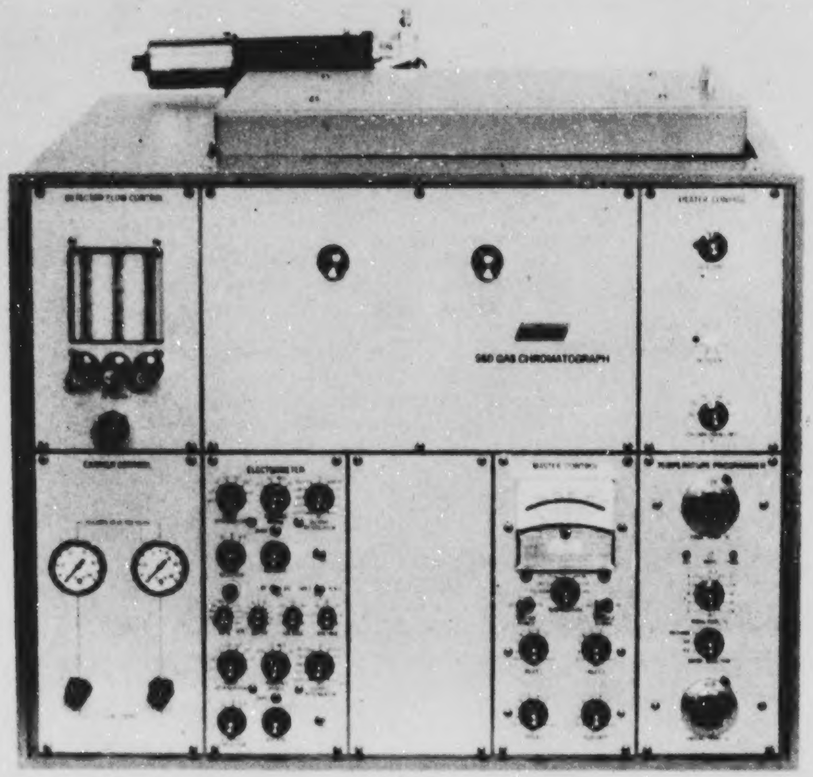
Option 4201-1400-3400-3400-2200-5104 + 113640-0001 ($6,390.) has standard simultaneous single column FPD detection for phosphorus and sulfur; simultaneous single column phosphorus and sulfur is also available

Address

Tracor Analytical Instruments
6500 Tracor Lane
Austin, TX 78721
(512) 926-2800   TWX 910-874-1372   Cable TRACOR

Halogen, Nitrogen or Sulfur Analyzer (Conductimetric)

Gas Chromatograph Model 113550-4201-1200-3102-220



Class	Laboratory: routine analysis/research
Principle of Operation	Gas Chromatography--Coulson Conductimetric Detection (GC-CCD)
Sensitivity	10^{-10}g chlorine, nitrogen or sulfur
Range	10^{-7} to 10^{-10} g chlorine, nitrogen or sulfur
Interferences	None, except for compounds containing the element being analyzed for.
Multiparameter Capability	Convertible by manufacturer's representative to: electron capture detection (ECD) for analysis of halogenated hydrocarbons (pesticides), flame photometric detection (FPD) for sulfur analysis, flame ionization detection (FID) for oil analyses, thermal conductivity detection (TCD) for gas analysis (sewage digester gas).
Sampling	Method: Syringe injected aliquot of pesticide sample onto glass GC column

Sample Inlet

Type: Silicone rubber septa, screw-cap retained on glass or stainless-steel injection ports
On-Column Injection: Available in 1/16", 1/8", and 1/4" sizes
Glass Liners (Inserts): Available in 1/8" and 1/4" sizes
Capillary Columns: Accessory steam-splitting injection port available for use with 1/16" tubing; 2 fixed-split ratios available 100/1 standard, 250/1 optional

Temperature Range: Ambient to 450°C
Temperature Regulation: Solid state, thermocouple feedback
Overheat Protection: Line fuse only

Column Oven

Type: Dual columns, injection ports and detectors; glass or metal columns, vertically coiled; forced air circulation
Carrier Gas: He or N_2, prepurified
  Flow control: independent differential flow regulators
  Flow range, tolerance; 2 to 200 cc/min He, ±0.3%
  Flow calibration: soap bubble flow meter standard, rotameters optional
Column Capacity: Standard, 1/8" O.D. metal tubing, 2 ea.: 50'
  Optional, 1/4" O.D. metal tubing, 2 ea.: 20'
  Accessory, 1/16" O.D. metal capillary, 2 ea.: ca. 200'
Temperature Range; Continuously adjustable, ambient to 400°C

Temperature Regulation: Fully proportional ±0.25°C
Overheat Protection: Adjustable limit switch
Optional Temperature Program: 49 linear rates, 1 to 50°C in 1° steps

Detector and Amplifier

Type: Coulson conductimetric with bridge controls
Temperature Range: Ambient to 900°C
Temperature Regulation: Variac
Overheat Protection: Line fuse only
Accessory Gas Flow: ca. 90 cc/min prepurified H_2 for halogen or nitrogen detection; ca. 90 cc/min prepurified O_2 for sulfur detection
Linear Dynamic Range: 10^3

Type: Solid state, Wheatstone bridge
Sensitivity: 1×10^{-12} A full scale
Linear Dynamic Range: 10^4
Cell voltage: 0-30 V DC
Drift: 1%/day at constant ambient

Noise:
Background Suppression: Coarse and fine adjustment

Attenuation: Output (attenuator), X1, X2, X4, . . .X1024

Outputs: For recorder, 1 mV; for computer 1 V

Time Constant: 0.3 sec maximum

Requirements

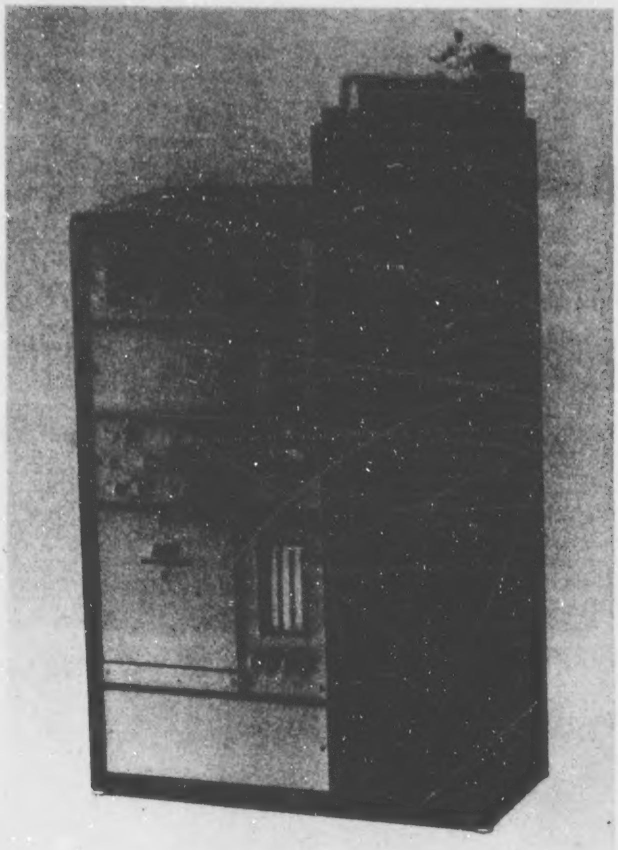
Recorder: 1 mV, servo-type, strip chart
Pressure Regulated Gas Supplies: 0 to 100 psig He; 0 to 60 psig H_2; 0 to 60 psig O_2; all gases, prepurified grade
Power: 117 V, 60 Hz (220 V, 50 Hz optional)
Size: 50.8 cm H, 60.2 cm W, 60.2 cm D (20" x 24" x 24")
Weight: 68 kg (150 lb)

References	Manufacturer's brochure "222 and 550 Series Gas Chromatograph" and price list APL-114 (1971)
Features	Complete with absorbents for interconversion between halogen, nitrogen and sulfur detection
Cost	Gas Chromatograph Model 550-(option) 4201-1400-3700 $4695.
Remarks	
Address	Tracor Analytical Instruments 6500 Tracor Lane Austin, TX 78721 (512) 926-2800 TWX 910-874-1372 Cable TRACOR

H2O-PES
Pesticide Analysis
Tracor 4
October 1973

Pesticide Analyzer (Electron Capture)

Gas Chromatograph Model 222



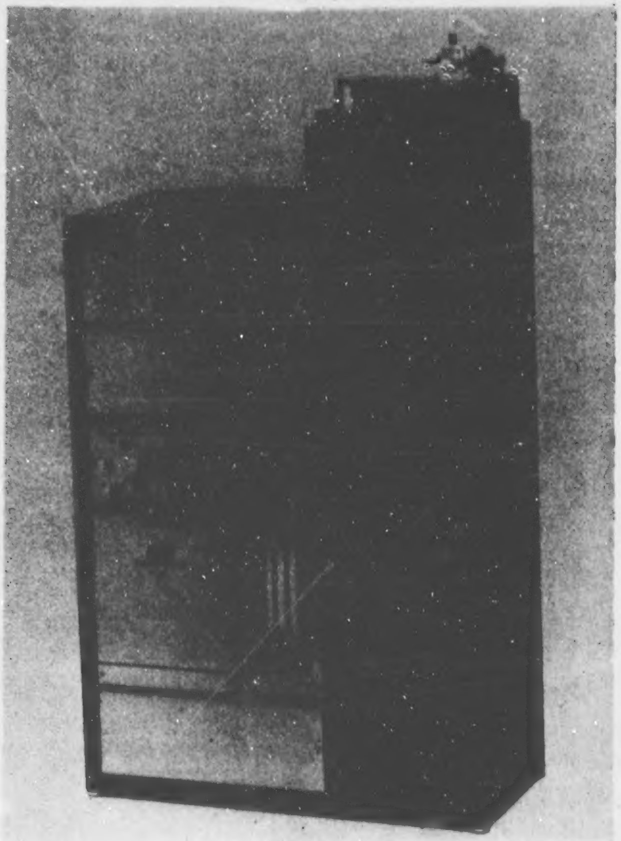
Class	Laboratory: routine analysis/research
Principle of Operation	Gas Chromatography--Electron Capture Detection (GC-ECD)
Sensitivity	10^{-12}g lindane ($C_6H_6Cl_6$)
Range	10^{-9} to 10^{-12}g lindane
Interferences	Appreciable interferences from: other halogenated and conjugated unsaturated organic compounds in general, also nitro and cyano groups Moderate interferences from: oxygenated or nitrogenous organics, O_2, H_2O GC column and septum bleed Slight or no interferences from: saturated hydrocarbons and fixed gases, among others.
Multiparameter Capability	Convertible by manufacturer's representative to: flame photometric detector (FPD) for phosphorus or sulfur analysis (pesticides), Coulson conductivity detector (CCD) specific for analysis of halogen, nitrogen or sulfur (pesticides), flame ionization detection (FID) for oil analysis, thermal conductivity detection (TCD) for gas analysis (sewage digester gas).
Sampling	Method: Syringe injected aliquot of pesticide sample onto glass GC column.

Sample Inlet	Type: Silicone rubber septa, screw-cap retained on 1/4" glass or stainless-steel injection ports On-Column Injection: 1/4" size Glass Liners (Inserts): Available in 1/4" size for biological samples
Column Oven	Type: Dual U-tube columns and injection ports; glass or metal columns, vertical U-tubes; forced air circulation Carrier Gas: 5% methane in argon or N_2 Flow control: independent differential flow regulators Flow range, tolerance: 2 to 200 cc/min He, ±0.3% Flow calibration: soap bubble flow meter and rotameters, standard Column capacity: Standard, 1/4" O.D. glass tubing, 2 ea.: 6' Optional, 1/4" O.D. metal tubing, 2 ea.: 20' Temperature range: Continuously adjustable, ambient to 400°C Temperature regulation: Fully proportional, ±0.25°C Overheat protection: Adjustable limit switch [Optional temperature program: 49 linear rates, 1 to 50°/C in 1° steps]
Detector	Type: High temperature electron capture (ECD), 15 millicuries Ni^{63} Temperature range: Ambient to 400°C Temperature regulation: Variac Overheat protection: Line fuse only Accessory gas flow: None required Linear dynamic range: Greater than 10
Detector Amplifier	Type: Pulsed frequency Sensitivity: 1×10^{-12} A full scale Linear dynamic range: 10^4 Drift: Noise: Background suppression: Attenuation: Input (range), X1, X10, X100, ...X1,000,000 Output (attenuator), X1, X2, X4, ...X1024 Outputs: For recorder, 1 mV; for computer 1 V Time constant: 0.3 sec maximum
Requirements	Recorder: 1 mV. servo-type, strip chart Pressure regulated gas supplies: 0 to 100 psig 5% methane in argon or N_2, prepurified grade Power: 117 V, 60 Hz (220 V, 50 Hz optional) Size: 154 cm H, 86 cm W, 42.5 cm D (56 1/2" x 33" x 17") Weight: 113 kg (250 lb)
Features	Vertical U-tube oven capable of accomodating four each 6' glass U-tube GC columns
Cost	Gas Chromatograph Model 222 with Electron Capture (Part no. 114400 - 4200 - 1400 - 3200N - 2100 - 5103) $
Remarks	Numerous other multiple column and detector options available
Address	Tracor Analytical Instruments 6500 Tracor Lane Austin, TX 78721 (512) 926-2800 TWX 910-874-1372 Cable TRACOR

H2O-PES
Pesticide Analysis
Tracor 5
October 1973

Pesticide Analyzer (Flame Photometric)

Gas Chromatograph Model 222

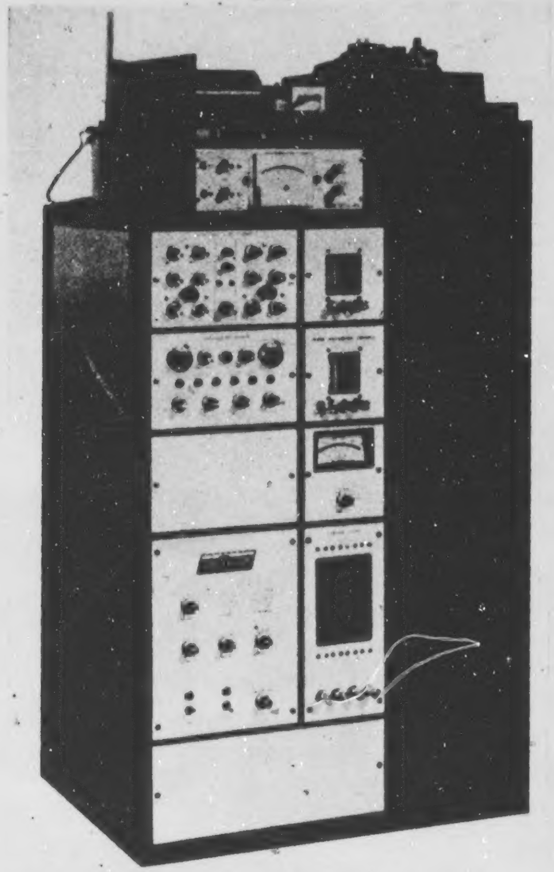


Class	Laboratory: routine analysis/research
Principle of Operation	Gas Chromatography - Flame Photometric Detection (GC-FPD)
Sensitivity	10^{-11} g phosphorus or sulfur
Range	10^{-6} to 10^{-11} g for phosphorus; 10^{-8} to 10^{-11} g for sulfur
Interferences	Slight interferences (0.01%) from organic compounds
Multiparameter Capability	Convertible by manufacturer's representative to: electron capture detection (ECD) for analysis of halogenated hydrocarbons (pesticides), Coulson conductivity detector (CCD) specific for analysis of halogen, nitrogen or sulfur, flame ionization detector (FID) for oil analysis, thermal conductivity detection (TCD) for gas analysis (sewage digester gas).
Sampling	Method: Syringe injected aliquot of pesticide sample onto glass GC column

Sample Inlet	Type: Silicone rubber septa, screw-cap retained on 1/4" glass or stainless-steel injection ports On-Column Injection: 1/4" size Glass Liners (Inserts): Available in 1/4" size for biological samples
Column Oven	Type: Dual U-tube columns and injection ports: glass or metal columns, vertical U-tubes; forced air circulation Carrier Gas: He or N_2, prepurified Flow control: independent differential flow regulators Flow range, tolerance: 2 to 200 cc/min He, ±0.3% Flow calibration: soap bubble flow meter and rotameters Column capacity: Standard, 1/4" O.D. glass U-tube 2 ea.: 6' Optional, 1/4" O.D. metal tubing, 2 ea.: 20' Temperature Range: Continuously adjustable, ambient to 400°C Temperature Regulation: Fully proportional ±0.25°C Overheat Protection: Adjustable limit switch [Optional temperature program: 49 linear rates, 1 to 50°/C in 1° steps]
Detector	Type: Independent or compensating dual flame ionization (FID) Temperature range: Ambient to 400°C Temperature regulation: Variac Overheat protection: Line fuse only Accessory gas flow: ca. 200 cc/min H_2; ca. 40 cc/min air; ca. 20 cc/min O_2; all gases prepurified Linear dynamic range: Greater than 10^6
Detector Amplifier	Type: Solid state, parametric design, dual channel Sensitivity: 1×10^{-12} A full scale Linear dynamic range: 10^6 Drift: 1%/day at constant ambient Noise: 1×10^{-14} A Background suppression: Three ranges, 0 to $\pm 10^{-6}$, 10^{-8}, 10^{-10} A with coarse and fine adjustment Attenuation: Input (range), X1, X10, X100, ...X1,000,000 Output (attenuator), X1, X2, X4, ...X1024 Outputs: For recorder, 1 mV; for computer 1 V Time constant: 0.3 sec maximum
Requirements	Recorder: 1 mV, servo-type, strip chart Pressure regulated gas supplies: 0 to 100 psig He; 0 to 100 psig H_2; 0 to 100 psig air; 0 to 30 psig O_2; all gases, prepurified grade Power: 117 V. 60 Hz (200 V, 50 Hz optional) Size: 154 cm H, 86 cm W, 42.5 cm D (56 1/2" x 33" x 17") Weight: 113 kg (250 lb)
Features	Vertical U-tube oven capable of accommodating four each 6' glass U-tube GC columns
Cost	Model 222 with Flame Photometer (Part no. 114400-4200-1400-3400H with 114390-0001 accessory) $6500.
Remarks	Numerous other multiple column and detector options available
Address	Tracor Analytical Instruments 6500 Tracor Lane Austin, TX 78721 (512) 926-2800 TWX 910-874-1372 Cable TRACOR

Pesticide Analyzer (Conductimetric)

Gas Chromatograph Model 222



Class	Laboratory: routine analysis/research
Principle of Operation	Gas Chromatography--Coulson Conductimetric Detection (GC-CCD)
Sensitivity	10^{-10} g chlorine, nitrogen or sulfur
Range	10^{-7} to 10^{-10} g chlorine, nitrogen or sulfur
Interferences	None, except for compounds containg the element being analyzed for.
Multiparameter Capability	Convertible by manufacturer's representative to: electron capture detection (ECD) for analysis of halogenated hydrocarbons (pesticides), flame photometric detection (FPD) for sulfur analysis, flame ionization detection (FID) for oil analyses, thermal conductivity detection (TCD) for gas analysis (sewage digester gas).
Sampling	Method: Syringe injected aliquot of pesticide sample onto glass GC column

Sample Inlet

Type: Silicone rubber septa, screw-cap retained on 1/4" glass or stainless-steel injection ports
On-Column Injection: 1/4" size
Glass Liners (Inserts): Available in 1/4" size for biological samples

Column Oven

Type: Dual U-tube columns and injection ports: glass or metal columns, vertical U-tubes; forced air circulation
Carrier Gas: He or N_2, prepurified
Flow control: independent differential flow regulators
Flow range, tolerance: 2 to 200 cc/min He, ±0.3%
Flow calibration: soap bubble flow meter and rotameters

Column Capacity: Standard, 1/4" O.D. glass U-tube, 2 ea.: 6'
Optional, 1/4" O.D. metal tubing, 2 ea.: 20'
Temperature Range: Continuously adjustable, ambient to 400°C

Temperature Regulation: Fully proportional ±0.25°C
Overheat Protection: Adjustable limit switch
[Optional temperature program: 49 linear rates, 1 to 50°/C in 1° steps]

Detector

Type: Coulson conductimetric with bridge controls
Temperature Range: Ambient to 900°C
Temperature Regulation: Variac
Overheat Protection: Line fuse only
Accessory Gas Flow: ca. cc/min prepurified H_2 for halogen or nitrogen detection; ca. cc/min prepurified O_2 for sulfur detection
Linear Dynamic Range: 10^3

Drift: 1%/day at constant ambient

Noise: 1×10^{-14} A
Background suppression: Three ranges, 0 to $\pm 10^{-6}$, 10^{-8}, 10^{-10} A with coarse and fine adjustment
Attenuation: Input (range), X1, X10, X100, ...X1,000,000
Output (attenuator), X1, X2, X4, ...X1024
Outputs: For recorder,, 1 mV; for computer 1 V

Time Constant: 0.3 sec maximum

Requirements

Recorder: 1 mV, servo-type, strip chart
Pressure Regulated Gas Supplies: 0 to 100 psig He; 0 to 60 psig H_2; 0 to 60 psig O_2; all gases, prepurified grade
Power: 117 V, 60 Hz (220 V, 50 Hz optional)
Size: 154 cm H, 86 cm W, 42.5 cm D (56 1/2" x 33" x 17")
Weight: 113 kg (250 lb)

Features

Vertical U-tube oven capable of accommodating four each 6' glass U-tube GC columns

Cost

Gas Chromatograph Model 222 with Conductimetric Detector (Part no. 114400-4200-1400-3700C) $6,700

Remarks

Numerous other multiple column and detector options available

Address

Tracor Analytical Instruments
6500 Tracor Lane
Austin, TX 78721
(512) 926-2800 TWX 910-874-1372 Cable TRACOR

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

H2O-PES
Pesticide Analysis
Varian Aerograph 1
October 1973

Halogenated Hydrocarbon Analyzer (ECD)

Gas Chromatograph Model 147520-00

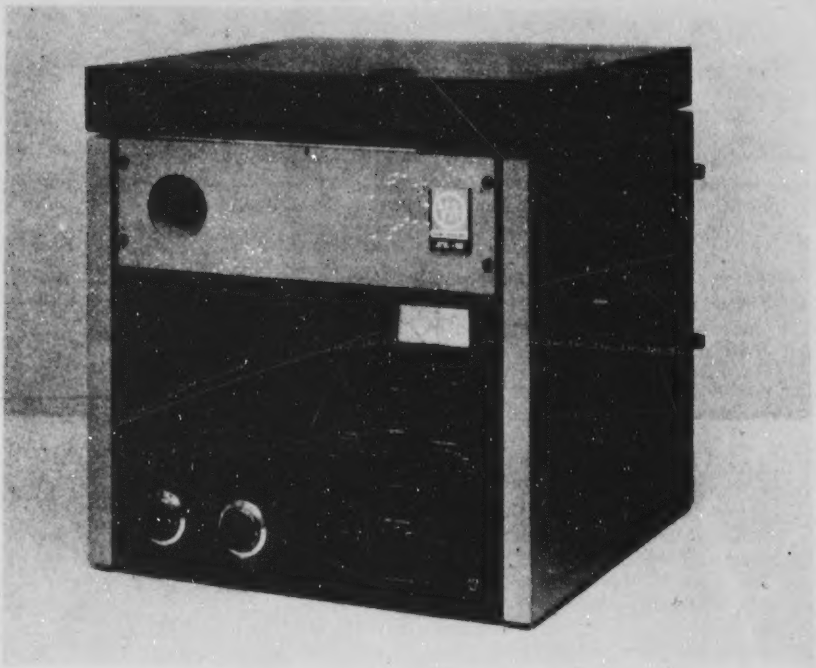
Class	Laboratory: routine analysis/research
Principle of Operation	Gas Chromatography - Electron Capture Detection (GC-ECD)
Sensitivity	10^{-13} g lindane ($C_6H_6Cl_6$)
Range	10^{-10} to 10^{-10} g lindane
Interferences	Appreciable interferences from: other halogenated and conjugated unsaturated organic compounds in general, also nitro and cyano groups Moderate interferences from: oxygenated or nitrogenous organics, O_2, H_2O Slight or no interferences from: GC column and septum bleed, saturated hydrocarbons and fixed gases, among others
Multiparameter Capability	Convertible by manufacturer's representative to thermionic detection (TID) for analysis of nitrogen or phosphorus (pesticides); flame ionization detection (FID) for oil analysis.
Sampling	Method: Syringe injected aliquot of pesticide sample onto glass GC column
Sample Inlet	Type: Silicone rubber septa, screw-cap retained on stainless-steel injection ports, 1/4" size (standard) On-column injection: 1/4" size Glass liners (inserts): Available in 1/8" size Temperature range: Ambient to 400°C Temperature regulation: Manually adjustable potentiometer Overheat protection: Line fuse only

Column Oven	Type: Single column, injection port and detector; glass or metal column, vertically coiled; thermostatted, forced air circulation Carrier gas: N_2 Flow control: optional differential flow regulator Flow range, tolerance: 10 to 150 cc/min N_2, ±1% Flow calibration: soap bubble flowmeter Column capacity: Standard, 1/4" O.D. glass tubing, 1 ea.: 3', 6', and 10' Optional, 1/8" O.D. metal tubing, 1 ea.: 50' Temperature range: Continuously adjustable, ambient to 400°C Temperature regulation: Fully proportional, ±0.2°C Overheat protection: Variable bimetallic temperature limit switch Optional temperature program: 10 linear rates, 0.5, 1, 2, 4, 6, 8, 10, 12, 15, 20 °C/min
Detector	Type: High temperature electron capture (ECD), 1 millicurie ScH^3 Temperature range: Ambient to Temperature regulation: Fully proportional, ±0.5°C Overheat protection: Optional temperature limit switch Accessory gas flow: none required Linear dynamic range: ca. 10^3
Detector Amplifier	Type: Solid state, JFET, single channel Sensitivity: 1×10^{-13} A full scale Linear dynamic range: 10^5: 10^8 with range switch Drift: Less than 1%/mo @ constant ambient Noise: Less than 1×10^{-14} A Background suppression: 0 to $\pm 9 \times 10^{-8}$ A with coarse and fine adjustment Attenuation: Input (range), X1, X10, X100, X1000 Output (attenuator), X1, X2, X4, ...X1024 Outputs: For recorder 1 mV; for integrator, computer, 1 V Time constant: 0.3 sec maximum
Requirements	Pressure regulated gas supplies: 0 to 100 psig N_2 Power: 117 V, 60 Hz (220 V, 50 Hz optional); 1700 W maximum Size: 42 cm H, 41 cm W, 41 cm D (16-1/2" x 16" x 16") Weight: 41 kg (89 ib)
References	a) Manufacturer's 1973 Chromatography Catalog
Features	Interchangeable modular components
Cost	Gas Chromatograph Model 145620-00 $3,275
Remarks	The 2100 series instruments feature standard vertical glass U-tube columns (Varian 3)
Address	Varian Aerograph 2700 Mitchell Drive Walnut Creek, CA 94598 (415) 939-2400 TWX 910-373-1731

H2O-PES
Pesticide Analysis
Varian Aerograph 2
October 1973

Phosphorus/Nitrogen Analyzer (TID)

Gas Chromatograph Model 148520-00



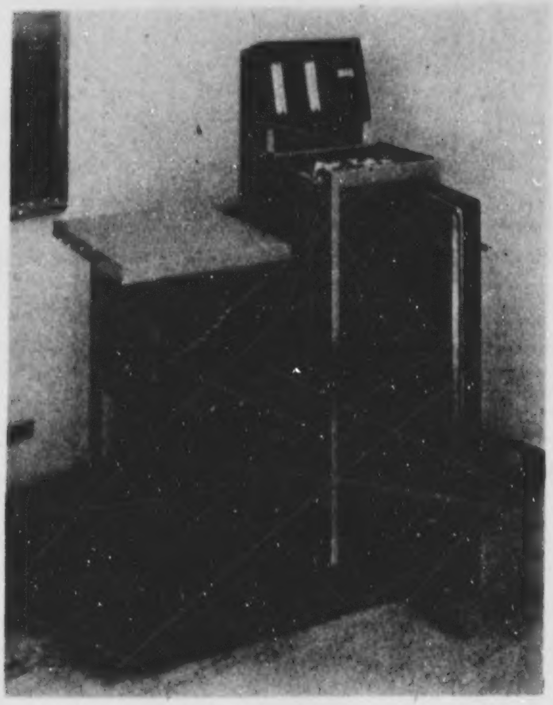
Class	Laboratory: routine analysis/research
Principle of Operation	Gas Chromatography - Thermionic Detection (GC-TID)
Sensitivity	10^{-13} g parathion (phosphorus); ca. 10^{-11} g for nitrogen containing compounds (e.g. Sevin)
Range	10^{-10} to 10^{-13} g parathion
Interferences	P vs C, 10,000: 1
Multiparameter Capability	Convertible by manufacturer's representative to electron capture detection (ECD) for analysis of halogenated hydrocarbons (pesticides);
Sampling	Method: Syringe injected aliquot of pesticide sample onto glass GC column
Sample Inlet	Type: Silicone rubber septa, screw-cap retained on stainless-steel injection ports, 1/4" size (standard) On-column injection: 1/4" size Glass liners (inserts): Available in 1/8" size Temperature range: Ambient to 400°C Temperature regulation: Manually adjustable potentiometer Overheat protection: Line fuse only

Column Oven	Type: Single column, injection port and detector; glass or metal column vertically coiled; thermostatted, forced air circulation Carrier gas: N_2 Flow control: optional differential flow regulator Flow range, tolerance: 10 to 150 cc/min N_2, ±1% Flow calibration: soap bubble flowmeter Column capacity: Standard, 1/4" O.D. glass tubing, 1 ea.: 3', 6', and 10' Optional, 1/8" O.D. metal tubing, 1 ea.: 50' Temperature range: Continuously adjustable, ambient to 400°C Temperature regulation: Fully proportional, ±0.2°C Overheat protection: Variable bimetallic temperature limit switch Optional temperature program: 10 linear rates, 0.5, 1, 2, 4, 6, 8, 10, 12, 15, 20 °C/min
Detector	Type: Thermionic (alkali flame) detector (TID) Temperature range: Ambient to 400°C Temperature regulation: Fully proportional, ±0.5°C Overheat protection: Optional temperature limit switch Accessory gas flow: ca. 30 cc/min prepurified H_2; ca. 350 cc/min prepurified air Linear dynamic range: Greater than 10^3
Detector Amplifier	Type: Solid state, JFET, single channel Sensitivity: 1×10^{-12} A full scale Linear dynamic range: 10^5 ; 10^8 with range switch Drift: Less than 1%/mo @ constant ambient Noise: Less than 1×10^{-14} A Background suppression: 0 to $9 \times 10^{-}$ A with coarse and fine adjustment Attenuation: Input (range), X1, X10, X100, X1000 Output (attenuator), X1, X2, X4, ...X1024 Outputs: For recorder 1 mV; for integrator, computer, 1 V Time constant: 0.3 sec maximum
Requirements	Pressure regulated gas supplies: 0 to 100 psig He; 0 to 30 psig H_2; 0 to 100 psig air; all gases, prepurified grade
References	a) Manufacturer's 1973 Chromatography Catalog
Features	Interchangeable modular components
Cost	Gas Chromatograph Model 148520-00 $2,925.
Remarks	The 2100 series instruments feature standard vertical glass U-tube columns (Varian 4)
Address	Varian Aerograph 2700 Mitchell Drive Walnut Creek, CA 94598 (415) 939-2400 TWX 910-373-1731

H2O-PES
Pesticide Analysis
Varian Aerograph 3
October 1973

Halogenated Hydrocarbon Analyzer ECD

Gas Chromatograph Model 210000-01 (Option 02-0007700-00)



Class	Laboratory: routine analysis/research
Principle of Operation	Gas Chromatography - Electron Capture Detection (GC-ECD)
Sensitivity	10^{-13} g lindane ($C_6H_6Cl_6$)
Range	10^{-10} to 10^{-13} g lindane
Interferences	Appreciable interferences from: other halogenated and conjugated unsaturated organic compounds in general, also nitro and cyano groups Moderate interferences from: oxygenated or nitrogenous organics, O_2, H_2O Slight or no interferences from: GC column and septum bleed, saturated hydrocarbons and fixed gases, among others
Multiparameter Capability	Convertible by manufacturer's representative to thermionic (alkali flame) detection of organic phosphorus or nitrogen (pesticides); flame ionization detection (FID) for oil analysis;
Sampling	Method: Syringe injected aliquot of pesticide sample onto glass GC column

Sample Inlet

Type: Silicone rubber septa, screw-cap retained on stainless-steel injection ports, 1/4" size (standard)
On-column injection: 1/4" size
Glass liners (inserts): Not available
Temperature range: Ambient to 400°C
Temperature regulation: Fully proportional, ±0.5°C
Overheat protection: Line fuse only

Column Oven

Type: Dual U-tube columns, injection ports and detectors; glass or metal columns, vertical U-tubes; thermostatted, forced air circulation
Carrier gas: N_2, prepurified
  Flow control: independent differential flow regulators
  Flow range, tolerance: 10 to 150 cc/min
  Flow calibration: soap bubble flowmeter
Column capacity: U-tube
  Standard, 1/4" O.D. glass tubing, 2 ea.: 3', 6', and 12'
  Optional, 1/4" O.D. metal tubing, 2 ea.: 50'
Temperature range: Continuously adjustable, ambient to 400°C
Temperature regulation: Fully proportional, ±0.5°C
Overheat protection: Variable bimetallic temperature limit switch
Temperature program: 10 linear rates, 0.5, 1, 2, 4, 6, 8, 10, 12, 15, 20 °C/min
Optional final isothermal timer: 0 to 99 min in 1 min steps
Optional initial isothermal timer: 0 to 99 min in 1 min steps
Cooling rate: 50°C/min

Detectors

Type: Independent dual high temperature electron capture (ECD), 1 millicurie ScH^3 each
Temperature range: Ambient to 400°C
Temperature regulation: Fully proportional, ±0.5°C
Overheat protection: Optional temperature limit switch
Accessory gas flow: ca. cc/min prepurified N_2
Linear dynamic range: 10^3; 10^8 with range switch

Detector Amplifiers

Type: Solid state, dual matched JFET (dual channel)
Sensitivity: 1×10^{-12} A full scale
Linear dynamic range: 10^5
Drift: Less than 1%/mo @ constant ambient
Noise: Less than 1×10^{-14} A
Background suppression: 0 to $\pm 9 \times 10^{-10}$ A with coarse and fine adjustment
Attenuation: Input (range), X1, X10, X100, X1000
  Output (attenuator), X1, X2, X4, ...X1024
Outputs: For recorder 1 mV; for integrator, computer, 1 V
Time constant: 0.3 sec maximum

Requirements

Pressure regulated gas supplies: 0 to 100 psig N_2, prepurified grade
Power: 220 V, 60 Hz, 4400 W maximum
Size: 170 cm H, 94 cm W, 61 cm D (67" x 37" x 24")
Weight: 132 kg (290 lb)

References

a) Manufacturer's 1973 Chromatography Catalog

Features

Dual independent detector amplifiers standard; instrument is expandable to four-column, four-independent-detector configuration

Cost

Gas Chromatograph Model 210000-01 (Option 96-000094-00) $5675

Remarks

Address

Varian Aerograph
2700 Mitchell Drive
Walnut Creek, CA 94598
(415) 939-2400 TWX 910-373-1731

INSTRUMENTATION FOR ENVIRONMENTAL MONITORING

H2O-PES
Pesticide Analysis
Varian Aerograph 4
October 1973

Phosphorus/Nitrogen Analyzer (TID)

Gas Chromatograph Model 210000-01 (Option 02-001352-00)

Class	Laboratory: routine analysis/research
Principle of Operation	Gas Chromatography - Thermionic (Alkali Flame) Detection (GC-TID)
Sensitivity	10^{-13} g parathion (phosphorus); ca. 10^{-11} g for nitrogen containing compounds (e.g. Sevin)
Range	10^{3} to 10^{-} g/sec
Interferences	P vs C, 10,000:1
Multiparameter Capability	Convertible by manufacturer's representative to electron capture detection (ECD) for analysis of halogenated hydrocarbons (pesticides);
Sampling	Method: Syringe injected aliquot of pesticide sample onto glass GC column

Sample Inlet	Type: Silicone rubber septa, screw-cap retained on stainless-steel injection ports, 1/4" size (standard) On-column injection: 1/4" size Glass liners (inserts): Not available Temperature range: Ambient to 400°C Temperature regulation: Fully proportional, ±0.5°C Overheat protection: Line fuse only
Column Oven	Type: Dual U-tube columns, injection ports and detectors; glass or metal columns, vertical U-tubes; thermostatted, forced air circulation Carrier gas: N_2, prepurified Flow control: independent differential flow regulators Flow range, tolerance: 10 to 150 cc/min Flow calibration: soap bubble flowmeter Column capacity: U-tube Standard, 1/4" O.D. Glass tubing, 2 ea.: 3', 6', and 12' Optional, 1/4" O.D. metal tubing, 2 ea.: 50' Temperature range: Continuously adjustable, ambient to 400°C Temperature regulation: Fully proportional, ±0.5°C Overheat protection: Variable bimetallic temperature limit switch Temperature program: 10 linear rates, 0.5, 1, 2, 4, 6, 8, 10, 12, 15, 20 °C/min Optional initial isothermal timer: 0 to 99 min in 1 min steps Optional final isothermal timer: 0 to 99 min in 1 min Cooling rate: 50°C/min
Detectors	Type: Independent or compensating dual thermionic (alkali flame) detectors (TID) Temperature range: Ambient to 400°C Temperature regulation: Fully proportional, ±0.5°C Overheat protection: Optional temperature limit switch Accessory gas flow: ca. 30 cc/min prepurified H_2; ca. 350 cc/min prepurified air per FID Linear dynamic range: ca. 10^3
Detector Amplifiers	Type: Solid state, dual matched JFET (dual channel) Sensitivity: 1×10^{-12} A full scale Linear dynamic range: 10^5; 10^8 with range switch Drift: Less than 1%/mo @ constant ambient Noise: Less than 1×10^{-14} A Background suppression: 0 to $\pm 9 \times 10^{-10}$ A with coarse and fine adjustment Attenuation: Input (range), X1, X10, X100, X1000 Output (attenuator), X1, X2, X4, ...X1024 Outputs: For recorder 1 mV; for integrator, computer, 1 V Time constant: 0.3 sec maximum
Requirements	Pressure regulated gas supplies: 0 to 100 psig He; 0 to 30 psig H_2; 0 to 100 psig air; all gases, prepurified grade
References	a) Manufacturer's 1973 Chromatography Catalog
Features	Dual independent detector amplifiers standard; instrument is expandable to four-column, four-independent-detector configuration
Cost	Gas Chromatograph Model 210000-01 (Option 02-001352-00) $5,340.
Remarks	
Address	Varian Aerograph 2700 Mitchell Drive Walnut Creek, CA 94598 (415) 939-2400 TWX 910-373-1731

13. Appendix 2

ENVIRONMENTAL PROTECTION AGENCY

[40 CFR Part 130]

ANALYSIS OF POLLUTANTS

Proposed Test Procedures

FEDERAL REGISTER, VOL. 38, NO. 125—FRIDAY, JUNE 29, 1973 17319

APPENDIX II

DETERMINATION OF ORGANOCHLORINE PESTICIDES IN INDUSTRIAL EFFLUENTS

1. *Scope and Application.* 1.1 This method covers the determination of various organochlorine pesticides, including some pesticidal degradation products and related compounds in industrial effluents. Such compounds are composed of carbon, hydrogen, and chlorine, but may also contain oxygen, sulfur, phosphorous, nitrogen or other halogens.

1.2 The following compounds may be determined individually by this method with a sensitivity of 1 µg/liter: BHC, lindane, heptachlor, aldrin, heptachlor, epoxide, dieldrin, endrin, Captan, DDE, DDD, DDT, methoxychlor, endosulfan, dichloran, mirex, pentachloronitrobenzene and trifluralin. Under favorable circumstances, Strobane, toxaphene, chlordane (technical grade) and others may also be determined. The usefulness of the method for other specific pesticides must be demonstrated by the analyst before any attempt is made to apply it to sample analysis.

1.3 When organochlorine pesticides exist as complex mixtures, the individual compounds may be difficult to distinguish. High, low, or otherwise unreliable results may be obtained through misidentification and/or one compound obscuring another of lesser concentration. Provisions incorporated in this method are intended to minimize the occurrence of such interferences.

2. *Summary.* 2.1 The method offers several analytical alternatives, dependent on the analyst's assessment of the nature and extent of interferences and/or the complexity of the pesticide mixtures found. Specifically, the procedure describes the use of an effective co-solvent for efficient sample extraction; provides, through the use of column chromatography and liquid-liquid partition, methods for elimination of nonpesticide interferences and the pre-separation of pesticide mixtures. Identification is made by selective gas chromatographic separations and may be corroborated through the use of two or more unlike columns. Detection and measurement is accomplished by electron capture, microcoulometric or electrolytic conductivity gas chromatography. Results are reported in micrograms per liter.

2.2 This method is recommended for use only by experienced pesticide analysts or under the close supervision of such qualified persons.

3. *Interferences.* 3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required (1).

3.2 The interferences in industrial effluents are high and varied and often pose great difficulty in obtaining accurate and precise measurement of organochlorine pesticides. Sample clean-up procedures are generally required and may result in the loss of certain organochlorine pesticides. Therefore, great care should be exercised in the selection and use of methods for eliminating or minimizing interferences. It is not possible to describe procedures for overcoming all of the interferences that may be encountered in industrial effluents.

3.3 Polychlorinated Biphenyls (PCB's): Special attention is called to industrial plasticizers and hydraulic fluids such as the PCB's which are a potential source of interference in pesticide analysis. The presence of PCB's is indicated by a large number of partially resolved or unresolved peaks which may occur throughout the entire chromatogram. Particularly severe PCB interference will require special separation procedures (2, 3).

3.4 Phthalate Esters: These compounds, widely used as plasticizers respond to the electron capture detector and are a source of interference in the determination of organochlorine pesticides using this detector. Water leaches these materials from plastics, such as polyethylene bottles and tygon tubing. The presence of phthalate esters is implicated in samples that respond to electron capture but not to the microcoulometric or electrolytic conductivity halogen detectors or to the flame photometric detector.

3.5 Organophosphorous Pesticides: A number of organophosphorous pesticides, such as those containing a nitro group, e.g., parathion, also respond to the electron capture detector and may interfere with the determination of the organochlorine pesticides. Such compounds can be identified by their response to the flame photometric detector (4).

4. *Apparatus and Materials.* 4.1 Gas Chromatograph—Equipped with glass lined injection port.

4.2 Detector Options:

4.2.1 Electron Capture—Radioactive (tritium or nickel 63).

4.2.2 Microcoulometric titration.

4.2.3 Electrolytic conductivity.

4.3 Recorder—Potentiometric strip chart (10 inch) compatible with the detector.

4.4 Gas Chromatographic Column Materials:

4.4.1 Tubing—Pyrex (180 cm long by 4 mm ID).

4.4.2 Glass Wool—Silanized.

4.4.3 Solid Support—Gas-Chrom Q (100–120 mesh).

4.4.4 Liquid Phases—Expressed as weight percent coated on solid support.

4.4.4.1 OV–1, 3%.

4.4.4.2 OV–210, 5%.

4.4.4.3 OV–17, 1.5% plus QF–1, 1.95%.

4.4.4.4 QF–1, 6% plus SE–30, 4%.

4.5 Kuderna-Danish (K–D) Glassware (Kontes).

4.5.1 Snyder Column—three ball (macro) and two ball (micro).

4.5.2 Evaporative Flasks—500 ml.

4.5.3. Receiver Ampuls—10 ml, graduated.

4.5.4 Ampul Stoppers.

4.6 Chromatographic Column—Chromaflex (400 mm long by 19 mm ID) with coarse fritted plate on bottom and Teflon stopcock; 250 ml reservoir bulb at top of column with flared out funnel shape at top of bulb (special order from Kontes K–420540–9011).

4.7 Chromatographic Column—Pyrex (approximately 400 mm long by 20 mm ID) with coarse fritted plate on the bottom.

4.8 Micro Syringes—10, 25, 50 and 100 μl.

4.9 Separatory Funnels—125 ml, 1000 ml and 2000 ml with Teflon stopcock.

4.10 Blender—High speed, glass or stainless steel cup.

4.11 Graduated cylinders—100 and 250 ml.

4.12 Florisil—PR Grade (60–100 mesh); purchase activated at 1250°F and store in the dark in glass containers with glass stoppers or foil lined screw caps. Before use, activate each in foil-covered glass container overnight in a bath at 130°C. Determine lauric-acid value as in section 13.

5. *Reagents, Solvents, and Standards.* 5.1 Ferrous Sulfate—(ACS) 30% solution in distilled water.

5.2 Potassium Iodide—(ACS) 10% solution in distilled water.

5.3 Sodium Chloride—(ACS) Saturated solution (pre-rinse NaCl with hexane) in distilled water.

5.4 Sodium Hydroxide—(ACS) 10 N in distilled water.

5.5 Sodium Sulfate—(ACS) Granular, anhydrous.

5.6 Sulfuric Acid—(ACS) Mix equal volumes of concentrated H_2SO_4 with distilled water.

5.7 Diethyl Ether—Nanograde, redistilled in glass, if necessary.

5.7.1 Must contain 2% alcohol and be free of peroxides by the following test: To 10 ml of ether in glass-stoppered cylinder previously rinsed with ether, add one ml of freshly prepared 10% KI solution. Shake and let stand for one minute. No yellow color should be observed in either layer.

5.7.2 Decompose ether peroxides by adding 40 g of 30% ferrous sulfate solution to each liter of solvent. *CAUTION:* Reaction may be vigorous if the solvent contains a high concentration of peroxides.

5.7.3 Distill deperoxidized ether in glass and add 2% methanol.

5.8 Acetonitrile, Hexane, Methanol, Methylene Chloride, Petroleum Ether (boiling range 30–60°C)—nanograde, redistill in glass if necessary.

5.9 Pesticide Standards—Reference grade.

6. *Calibration.* 6.1 Gas chromatographic operating conditions are considered acceptable if the response to dicapthon is at least 50% of full scale when ≤ 0.06 ng is injected for electron capture detection and ≤ 100 ng is injected for microcoulometric or electrolytic conductivity detection. For all quantitative measurements the detector noise level should be less than 2% of full scale and be operated within its linear response range.

6.2 Standards are injected frequently as a check on the stability of operating conditions. Gas chromatograms of several standard pesticides are shown in Figures 1, 2, 3 and 4 and provide reference operating conditions for the four recommended columns.

6.3 The elution order and retention ratios of various organochlorine pesticides are provided in Table 1 as a guide.

7. *Quality Control.* 7.1 Duplicate and spiked sample analyses are recommended as quality control checks. When the routine occurrence of a pesticide is being observed, the use of quality control charts are recommended (5).

7.2 Each time a set of samples is extracted, a method blank is determined on a volume of distilled water equivalent to that used to dilute the sample.

8. *Sample Preparation.* 8.1 Blend the sample if suspended matter is present and adjust pH to near neutral (pH 6.5–7.5) with 50% sulfuric acid or 10 N sodium hydroxide.

8.2 For a sensitivity requirement of 1 μg/1, when using microcoulometric or electrolytic conductivity methods for detection take 100 ml of sample for analysis. If interferences pose no problem, the sensitivity of the electron capture detector should permit as little as 50 ml of sample to be used. Background information on the extent and nature of interferences will assist the analyst in choosing the required sample size and preferred detector.

8.3 Quantitatively transfer the proper aliquot into a two-liter separatory funnel and dilute to one liter.

9. *Extraction.* 9.1 Add 60 ml of 15% methylene chloride in hexane (v/v) to the sample in the separatory funnel and shake vigorously for two minutes.

9.2 Allow the mixed solvent to separate from the sample, then draw the water into a one-liter Erlenmeyer flask. Pass the organic layer through a column containing 3 to 4 inches of anhydrous sodium sulfate, and collect it in a 500 ml K–D flask equipped with a 10 ml ampul. Return the water phase to the separatory funnel. Rinse the Erlenmeyer flask with a second 60 ml volume of solvent; add the solvent to the separatory funnel and complete the extraction procedure a second time. Perform a third extraction in the same manner.

9.3 Concentrate the extract in the K–D evaporator on a hot water bath.

9.4 Analyze by gas chromatography unless a need for cleanup is indicated, see Section 10.

10. *Clean-up and Separation Procedures.* 10.1 Interferences in the form of distinct peaks and/or high background in the initial gas chromatographic analysis, as well as, the physical characteristics of the extract (color, cloudiness, viscosity) and background knowledge of the sample will indicate whether clean-up is required. When these interfere with measurement of the pesticides, or effect column life or detector sensitivity, proceed as directed below.

10.2 Acetonitrile Partition—This procedure is used to remove fats and oils from the sample extracts. It should be noted that not all pesticides are quantitatively recovered by this procedure. The analyst must be aware of this and demonstrate the efficiency of the partitioning for specific pesticides. Of the pesticides listed in Section 1.2 only mirex is not efficiently recovered.

10.2.1 Quantitatively transfer the previously concentrated extract to a 125 ml separatory funnel with enough hexane to bring the final volume to 15 ml. Extract the sample four times by shaking vigorously for one minute with 40 ml portions of hexane-saturated acetonitrile.

10.2.2 Combine and transfer the acetonitrile phases to a one-liter separatory funnel and add 650 ml of distilled water and 40 ml of saturated sodium chloride solution. Mix thoroughly for 30 to 45 seconds. Extract with two 100 ml portions of hexane by vigorously shaking about 15 seconds.

10.2.3 Combine the hexane extracts in a one-liter separatory funnel and wash with two 100 ml portions of distilled water. Discard the water layer and pour the hexane layer through a 3 to 4 inch anhydrous sodium sulfate column into a 500 ml K–D flask equipped with a 10 ml ampul. Rinse the separatory funnel and column with three 10 ml portions of hexane.

10.2.4 Concentrate the extracts to 6 to 10 ml in the K–D evaporator in a hot water bath.

10.2.5 Analyze by gas chromatography unless a need for further cleanup is indicated.

10.3 Florisil column adsorption chromatography.

10.3.1 Adjust the sample extract volume to 10 ml.

10.3.2 Place a charge of activated Florisil (weight determined by lauric-acid value, as described in Section 13) in a Chromaflex column. After settling the Florisil by tapping the column, add about one-half inch layer of anhydrous granular sodium sulfate to the top.

10.3.3 Pre-elute the column, after cooling, with 50 to 60 ml of petroleum ether. Discard the eluate and just prior to exposure of the sulfate layer to air, quantitatively transfer the sample extract into the column by decantation and subsequent petroleum ether washings. Adjust the elution rate to about 5 ml per minute and, separately, collect up to three eluates in 500 ml K–D flasks equipped with 10 ml ampuls (see Section 10.4). Perform the first elution with 200 ml of 6% ethyl ether in petroleum ether, and the second elution with 200 ml. of 15% ethyl ether in petroleum ether. Perform the third elution with 200 ml of 50% ethyl ether in petroleum ether and the fourth elution with 200 ml of 100% ethyl ether.

10.3.4 Concentrate the eluates to 6–10 ml in the K–D evaporator in a hot water bath.

10.3.5 Analyze by gas chromatography.

10.4 Eluate Composition—By using an equivalent quantity of any batch of Florisil as determined by its lauric acid value, the pesticides will be separated into the eluates indicated below:

6% Eluate. Aldrin, BHC, Chlordane, DDD, DDE, DDT, Heptachlor, Heptachlor Epoxide, Lindane, Methoxychlor, Mirex Pentachloronitrobenzene, Strobane, Toxaphene, Trifluralin, and PCB's.

15% Eluate. Endosulfan I, Endrin, Dieldrin, Dichloran, Phthalate esters.

50% Eluate. Endosulfan II, Captan.

Certain thiophosphate pesticides will occur in each of the above fractions, as well as the 100% fraction. For additional information regarding eluate composition, refer to the FDA Pesticide Analytical Manual (6).

11. *Calculation of Results.* 11.1 Determine the pesticide concentration by using the absolute calibration procedure described below or the relative calibration procedure as described in reference 1.

11.2 Micrograms/liter $= \frac{(A)\ (B)\ (V_t)}{(V_i)\ (V_s)}$

Where A = ng standard/Standard area, B = Sample aliquot area, V_i = Volume of extract injected (μl), V_t = Volume of total extract (μl), and V_s = Volume of water extracted (ml).

12. *Reporting Results.* 12.1 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analysed, all data obtained should be reported.

13. *Standardization of Florisil Column by Weight Adjustment Based on Absorption of*

Lauric Acid. 13.1 A rapid method for determining adsorptive capacity of Florisil is based on adsorption of lauric acid from hexane solution (6, 7). An excess of lauric acid is used and amount not adsorbed is measured by alkali titration. Weight of lauric acid adsorbed is used to calculate, by simple proportion, equivalent quantities of Florisil for batches having different adsorptive capacities.

13.2 Apparatus: 13.2.1 Buret, 25 ml volume with 1/10 ml graduations.

13.2.2 Erlenmeyer flasks, 125 ml volume with narrow mouth and 25 ml volume, glass stoppered.

13.2.3 Pipet, 10 and 20 ml transfer.

13.2.4 Volumetric flasks, 500 ml volume.

13.3 Reagents and Solvents.

13.3.1 Alcohol, ethyl, USP or absolute, neutralized to phenolphthalein.

13.3.2 Hexane, distilled from all glass apparatus.

13.3.3 Lauric acid, purified, CP.

13.3.4 Lauric acid solution. Transfer 10.000 grams lauric acid to a 500 ml volumetric flask, dissolve in hexane, and dilute to 500 ml (1ml = 20 mg).

13.3.5 Phenolphthalein indicator. Dissolve 1 gram in alcohol and dilute to 100 ml.

13.3.6 Sodium hydroxide. Dissolve 20 grams NaOH (pellets, reagent grade) in water and dilute to 500 ml (1 N). Dilute 25 ml 1 N NaOH to 500 ml with water (0.05 N). Standardize as follows: Weigh 100 to 200 mg lauric acid into 125 ml Erlenmeyer flask. Add 50 ml neutralized ethyl alcohol and 3 drops phenolphthalein indicator; titrate to permanent end point. Calculate mg lauric acid/ml 0.05 N NaOH (about 10 mg/ml).

13.4 Procedure: 13.4.1 Transfer 2,000 grams of Florisil to 25 ml glass stoppered Erlenmeyer flasks. Cover loosely with aluminum foil and heat overnight at 130°C. Stopper, cool to room temperature, add 20.0 ml of lauric acid solution (400 mg), stopper, and shake occasionally for 15 minutes. Let adsorbent settle and pipet 10.0 ml of supernatant into a 125 ml Erlenmeyer flask. Avoid inclusion of any Florisil. 13.4.2 Add 50 ml neutral alcohol and 3 drops indicator solution; titrate with 0.05 N NaOH to a permanent end point

13.5 Calculation of Lauric Acid Value, and adjustment of column weight.

13.5.1 Calculate the amount of lauric acid adsorbed on the Florisil as follows: Lauric Acid Value = mg lauric acid/grams of Florisil = 200—(ml required for titration of X mg lauric acid/ml of 0.05 N NaOH).

13.5.2 To obtain an equivalent quantity of any batch of Florisil, divide 110 by lauric acid value for that batch and multiply by 20 grams. Verify proper elution of pesticides by Section 13.6 .

13.6 Test for Proper Elution Pattern and Recovery of Pesticides: Prepare a test mixture containing aldrin, heptachlor epoxide, p, p'-DDE, dieldrin, Parathion and malathion. Dieldrin and Parathion should elute in the 15% eluate; all but a trace of malathion in the 50% eluate, and the others in the 6% eluate.

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1. "Method for Organic Pesticides in Water and Wastewater," (1971) Environmental Protection Agency, National Environmental Research Center, Cincinnati, Ohio 45268.

2. Monsanto Methodology for Aroc lors—Analysis of Environmental Materials for Polychlorinated Biphenyls, Analytical Chemistry Method 71-35, (1970) Monsanto Company, St. Louis, Missouri 63166.

3. "Method for Polychlorinated Biphenyls in Industrial Effluents." (1973) Environmental Protection Agency, National Environmental Research Center, Cincinnati, Ohio 45268.

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5. "Handbook for Analytical Quality Control in Water and Wastewater Laboratory", (1972) Chapter 6, Section 6.4, U.S. Environmental Protection Agency, National Environmental Research Center, Analytical Quality Control Laboratory, Cincinati, Ohio 45268.

6. "Pesticide Analytical Manual", U.S. Dept. of Health, Education and Welfare, Food and Drug Administration, Washington, D.C.

7. Mills, P. A., "Variation of Florisil Activity: Simple Method for Measuring Adsorbent Capacity and its Use in Standardizing Florisil Columns", *Journal of the Association of Official Analytical Chemists, 51*, 29 (1968).

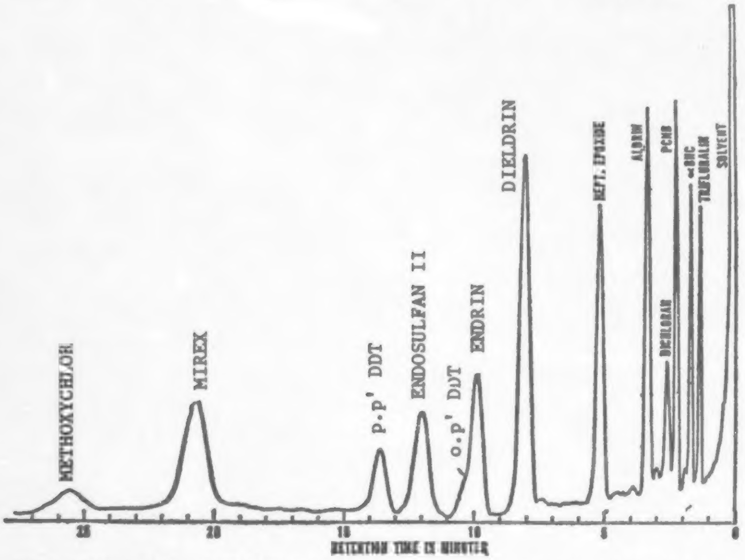

Figure 1. Column Packing: 1.5% OV-17 + 1.95% QF-1, Carrier Gas: Argon/Methane at 60 ml/min, Column Temperature: 200 C., Detector: Electron Capture.

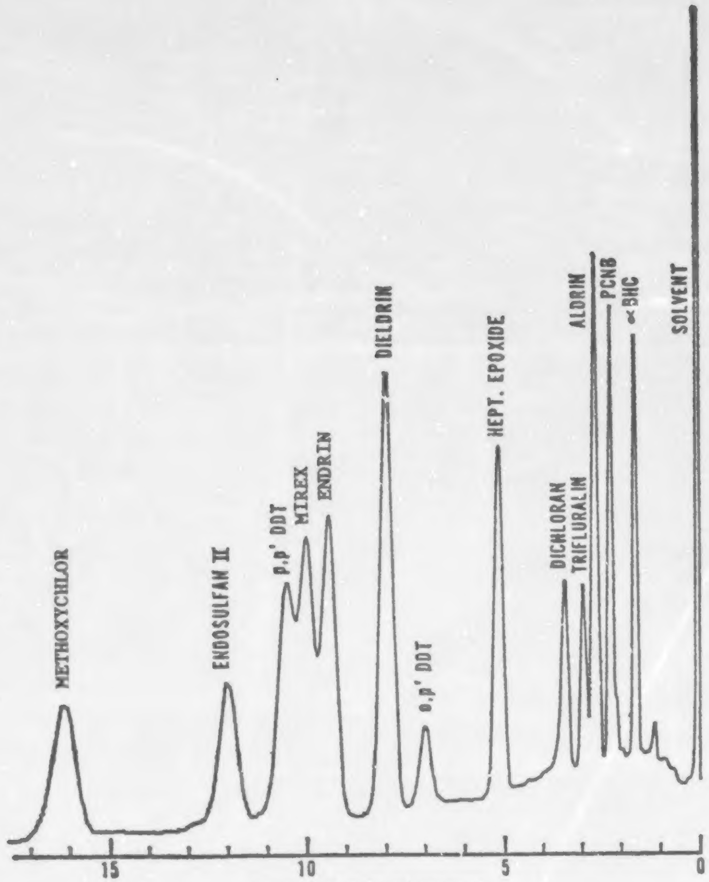

Figure 2. Column Packing: 5% OV-210, Ca rier Gas: Argon/Methane at 70 ml/min, Column Temperature: 180 C, Detector: Electron Capture.

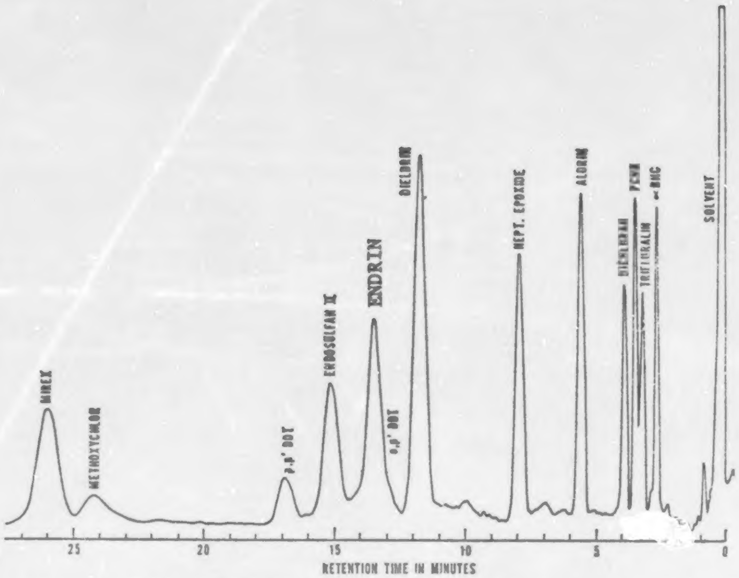

Figure 3. Column Packing: 6% QF-1 + 4% SE-30, Carrier Gas: Argon/Methane at 60 ml/min, Column Temperature: 200 C, Detector: Electron Capture.

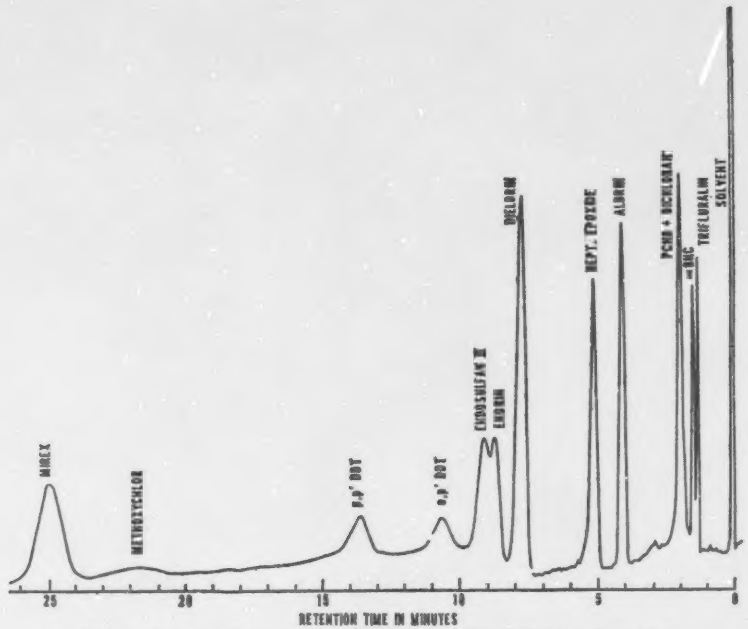

Figure 4. Column Packing: 3% OV-1, Carrier Gas: Argon/Methane at 70 ml/min, Column Temperature: 180 C, Detector: Electron Capture.

TABLE 1.—*Retention ratios of various organochlorine pesticides to aldrin*

Liquid Phase[1]	1.5% OV-17 + 2.95% QF-1	5% OV-210	3% OV-1	6% QF-1 + 4% SE-30
Column Temp	200 C	180 C	180 C	200 C
Argon/Methane Carrier Flow	60 ml/min	70 ml/min	70 ml/min	60 ml/min
Pesticide	RRt	RRt	RRt	RRt
Trifluralin	0.39	1.11	0.33	0.57
α-BHC	0.54	0.64	0.35	0.49
PCNB	0.68	0.85	0.49	0.63
Lindane	0.69	0.81	0.44	0.60
Dichloran	0.77	1.29	0.49	0.70
Heptachlor	0.82	0.87	0.78	0.83
Aldrin	1.00	1.00	1.00	1.00
Heptachlor Epoxide	1.54	1.93	1.28	1.43
Thiodan I	1.95	2.48	1.62	1.79
p,p'-DDE	2.23	2.10	2.00	1.82
Dieldrin	2.40	3.00	1.93	2.12
Captan	2.59	4.09	1.22	1.94
Endrin	2.93	3.56	2.18	2.42
o,p'-DDT	3.16	2.70	2.69	2.39
p,p'-DDD	3.48	3.73	2.61	2.55
Thiodan II	3.59	4.59	2.25	2.72
p,p'-DDT	4.18	4.07	3.50	3.12
Mirex	6.1	3.78	6.6	4.79
Methoxychlor	7.6	6.5	5.7	4.60
Aldrin (Min. absolute)	3.5	2.6	4.0	5.6

[1] All columns glass, 180 cm x 4 mm ID, solid support Gas-Chrom Q (100/120 mesh).

[FR Doc.73-12967 Filed 6-28-73;8:45 am]

Phenolics
PHE

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FOR

INSTRUMENTATION FOR MONITORING PHENOLICS

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Appendix

A. INTRODUCTION

Phenols are a family of organic compounds characterized by the presence of a benzene ring bearing a hydroxyl group. The simplest molecule in this series is phenol itself (Fig. A-1).

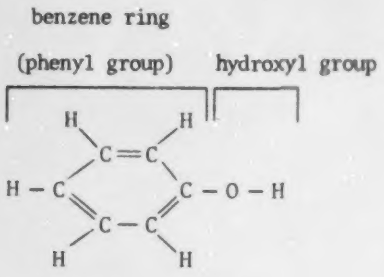


FIGURE A-1. Phenol: molecular configuration of atoms.

The family or series of phenolic compounds results from the variety of substitutions available for the hydrogen atoms on the ring. An indefinite number of compounds are possible which are phenolic in a chemical sense, although they may otherwise differ widely in their properties.

1. Nomenclature and Notation

Organic chemists customarily abbreviate the above chemical notation by omitting the benzene carbon and hydrogen atoms (Fig. A-2):

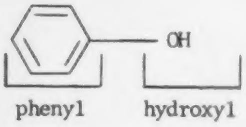
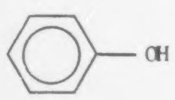


FIGURE A-2. Phenol: simplified notation.

The alternating double and single lines of the hexagon formally represent double and single bonds between the carbon atoms. However, these bonds are virtually equivalent in most benzenoid compounds; hence, their special nature is sometimes also indicated as follows:



Occasionally benzene rings have been indicated by simple hexagons; however, this practice should be reserved for saturated (cyclohexane) rings.

In the above diagrams phenol can be considered to consist of two functional groups: the benzene ring and the hydroxyl. As a functional group the benzene ring less one hydrogen atom is commonly referred to as a phenyl group or radical. Frequently phenyl is abbreviated as Ph or the Greek equivalent, ϕ. Thus, PhOH and ϕOH are alternative expressions for phenol. Benzenoid compounds are also known inexactly as aromatic compounds. When used as a functional group in a more general sense, the benzenoid group may also be called an aryl substituent and abbreviated as Ar. Thus, ArOH is a general expression for phenolic compounds which includes various substitutions for the hydrogens on the phenyl group (benzene ring).

Substitution for one or more of the hydrogens on the ring leads to a diverse variety of phenolics. When the substituent is a single methyl group (-CH_3) the phenolic is called a cresol. As shown in Figure A-3, three different chemical structures are possible depending on which hydrogen is substituted. Although these three compounds are similar in many physical and chemical properties, they are not identical. Early convention employed the Greek terms, *ortho*-, *meta*- and *para*-, to indicate the position of the methyl substituent as adjacent, intermediate or opposite to the phenolic hydroxyl position. This system persists widely among the more elementary substituted phenols and has been abbreviated to *o*-, *m*- and *p*-, respectively, to indicate the three structural isomers (Fig. A-3).

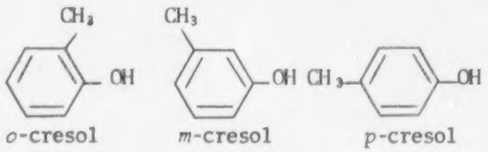
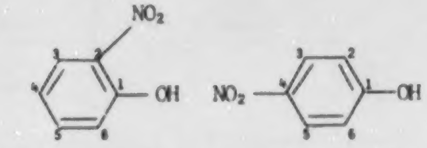


FIGURE A-3. Isomeric cresols.

The methylphenols (cresols) were known and used before their chemical structures were established. They were obtained mainly from fractional distillation of coal tar. If they had been derived synthetically directly from phenol they probably would have been named methylphenols as have been other derived compounds such as the nitrophenol isomers (Fig. A-4).



o-nitrophenol p-nitrophenol

FIGURE A-4. Isomeric nitro substituted phenols.

Nomenclature based on numbering of the benzene ring is also employed. If the compound is named as a substituted phenol, the ring carbon bearing the phenolic hydroxyl is designated C_1. Thus o-nitrophenol ≡ 2-nitrophenol and p-nitrophenol ≡ 4-nitrophenol, and so forth. Of course, multiple substitution is possible, e.g., the potent disinfectant, 2,3,4,5,6-pentachlorophenol (Fig. A-5).

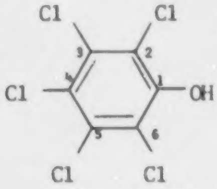
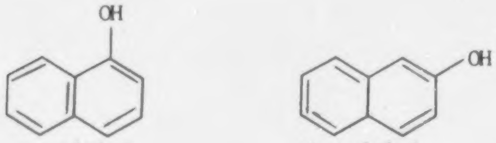


FIGURE A-5. Pentachlorophenol.

As chemical structures become more complex, particularly those of naturally occuring phenolics, it becomes convenient to use a numbering system based on one of the larger molecules. For example, hydroxylated naphthalenes are phenolic compounds called naphthols which exist in two unsubstituted structural configurations -- α- and β- (Fig. A-6).



α-naphthol β-naphthol

FIGURE A-6. Isomeric naphthols.

Substituted naphthols are better described according to the naphthalene ring numbering system, e.g., 4,6-dimethyl-1-naphthol (Fig. A-7).

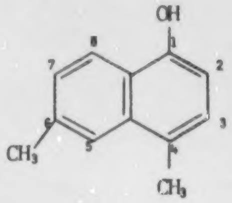


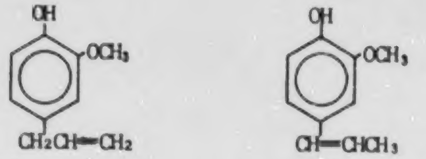
FIGURE A-7. 4,6-dimethyl-1-naphthol.

Additional information is available from most elementary organic chemistry textbooks (e.g., Ref. 1-3).

2. Historical Aspects

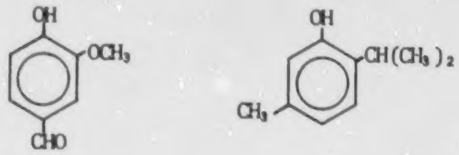
Man's relationship with phenolic compounds is lengthy and diverse (Ref. 1-4). Phenol (Fig. A-1) and its monomethyl substituted analogs, the cresols (Fig. A-2), have been used as biocides from the early days of microbiology. These elementary phenols were readily available in crude form from distillates of wood, coal and petroleum tars under the names of creosote, cresylic acid and tar acids. Wood tar creosote was once used as an antiseptic, whereas coal tar creosote has been employed to protect wooden telephone poles, railroad ties, etc., from termites and fungi. Such wood is now treated with pentachlorophenol (Fig. A-5). The potency of antiseptics is still evaluated in comparison with the effect of a 5% aqueous solution of phenol on Staphylococcus aureus. The disinfectant, hexachlorophene, is a phenolic once widely used in hospitals and in bath soap but now sharply curtailed by the FDA.

Besides being poisonous in gram quantities, simple phenols when diluted (e.g., mg/l) manifest an objectionable taste which can render food or drinking water unpalatable. On the other hand, several naturally occurring substituted phenols are important as flavoring ingredients, e.g., eugenol, isoeugenol, vanillin and thymol (Fig. A-8).



Eugenol — *Oil of cloves*

Isoeugenol — *Oil of nutmeg*



Vanillin — *Vanilla bean*

Thymol — *Oil of thyme and mint*

FIGURE A-8. Phenolics related to spice flavors or odors (from Ref. 1).

Natural polyphenolics make up the complex tannins extracted from tree bark to cure (tan) leather. Hydrolysis or fermentation of gallotannin yields a polyphenolic, gallic acid (Fig. A-9) as a major constituent. When subjected to heat, gallic acid loses CO_2 to form the trihydric phenol, pyrogallol, a photographic developer.

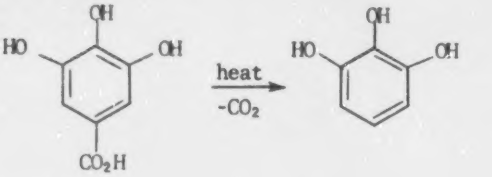


FIGURE A-9. Gallic acid converted to pyrogallol (from Ref. 2).

Phenols have a substantial history as the synthetic source for pharmaceuticals (e.g., aspirin, phenolphthalein), pesticides (2,4-D; 2,4,5-T), fibers (nylon-6), resins (Bakelite, Formica, plywood adhesives, epoxies), anti-oxidants (BHT, BHA), photographic developers and numerous dyes, to name a few. After World War I, large scale commercial synthesis of phenol itself was necessary to meet the demand for phenolic resins. Recent production figures are shown in Table A-1.

TABLE A-1.

U.S. Phenol Production, 1000 lb (from Ref. 4)

Year	Synthetic	Natural
1950	291,887	20,220
1955	475,003	41,676
1960	730,654	42,052
1965	1,173,441	55,672

3. Characteristics

A large number of phenols arise from both natural (biological and geological) and synthetic sources. Examples listed in Table A-2 are but a fraction of those which have been characterized. As Table A-2 indicates, phenols range from moderately volatile compounds (e.g., phenol, b.p. 182°C) to the relatively involatile (e.g., pentachlorophenol, b.p. 310°C). The lowest molecular weight compounds (phenol, the cresols, dimethylphenols or xylenols and ethylphenols) have a characteristically pungent, antiseptic odor and taste. As the number, size and variety of substituents increases, organoleptic (taste and odor) perception of phenols varies and in some cases becomes esthetically pleasing in modest concentrations rather than objectionable (see Fig. A-8). In general, organoleptic perception of phenols declines with increasing molecular weight and decreasing volatility.

3.1 Hydrogen Bonding

Another characteristic of phenols is their moderate solubility in water. The

TABLE A-2.

Physical Properties of Selected Phenols.

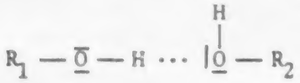
Nonstandard Temperatures or Pressures Indicated in Subscript Parentheses.

Name	Melting Point, °C (Ref. 5)	Boiling Point, °C (Ref. 5)	Solubility g/100g H_2O (20°C) (Ref. 5)	Acid Dissociation Constant, $K_a \times 10^{-10}$ (H_2O, 25°C) (Ref. 6)
Phenol (Fig. A-1, A-2)	41	182	$9.3_{(25^\circ C)}$	1.28
o-Cresol (Fig. A-3)	31	191	2.5	0.63
m-Cresol (Fig. A-3)	12	203	0.5	0.98
p-Cresol (Fig. A-3)	35	202	1.8	0.67
o-Chlorophenol	7(α)	176	2.9	32
m-Chlorophenol	33	214	2.6	14
p-Chlorophenol	43	217	2.7	6.6
2,4-Dichlorophenol	45	210	0.45	18
2,3,4,5,6-Pentachlorophenol (Fig. A-5)	191	310	$0.003_{(50^\circ C)}$	5500
o-Nitrophenol (Fig. A-4)	45	$100^{a}_{(0.1\ atm)}$	0.2	680
m-Nitrophenol	97	$194^{a}_{(0.1\ atm)}$	1.4	53
p-Nitrophenol (Fig. A-4)	114	279^{a} decomp. (0.1 atm)	$1.6_{(25^\circ C)}$	690
2,4-Dinitrophenol	113	—	$0.14_{(55^\circ C)}$	1.1×10^{6}
2,4,6-Trinitrophenol (Picric acid)	122	explodes > 300°	1.23	4.2×10^{9}
1,2-Dihydroxybenzene (Catechol)	105	246	$45^{a}_{(25^\circ C)}$	3.3^{b}
1,3-Dihydroxybenzene (Resorcinol)	110	276	$123^{a}_{(25^\circ C)}$	3.6^{b}
1,4-Dihydroxybenzene (Hydroquinone)	172	285	$8^{a}_{(25^\circ C)}$	$0.45^{b}_{(20^\circ)}$
1,2,3-Trihydroxybenzene (Pyrogallol: Fig. A-9)	134	309	$40_{(13^\circ C)}$	∿1000

[a] Reference 1

[b] Reference 2

presence of the hydroxyl group differentiates phenol (ϕOH) from benzene (ϕH) and accounts for phenol's greater water solubility: 7% vs. 0.07% for benzene, at 20°C. This "hydrophilic" character is the result of a phenomenon called "hydrogen bonding" which occurs widely in nature. For example, it is the reason given for the relatively high boiling point of water (HOH) and its unequaled heat of vaporization. In this case hydrogen bonding is a weak association of the oxygen-bonded hydrogen nucleus (proton) of the hydroxyl with the unbonded electron pair of an oxygen from another hydroxyl group as indicated by the dotted line in Figure A-10.



$$R_1 - \overline{\underline{O}} - H \cdots |\overset{\displaystyle H}{\underline{O}} - R_2$$

FIGURE A-10. Schematic of hydrogen bonding.

Solid lines between letters (atoms) indicates two-electron covalent bonds. Solid lines around oxygen atoms (O's) indicates unbonded electron pairs (orbitals). Dotted line between hydrogen atom (H) and unbonded oxygen electron pair indicates the hydrogen bond. R_1 and R_2 indicates any covalently bonded atom, e.g., C, H. Where $R_1 = R_2 = H$ the example is hydrogen bonding between two water (HOH) molecules. Where $R_1 = \phi$ (phenyl) and $R_2 = H$, the example indicates hydrogen bonding between phenol (ϕOH) and water (HOH).

Additional hydroxyl substituents further enhance the water solubility of phenolics (see Table A-2). On the other hand, increasing size and number of hydrocarbon (alkyl, cycloalkyl, aryl) substituents decreases the solubility in water by making the phenolic more oil-like (hydrophobic). When phenols are substituted *ortho* to the hydroxyl with polar* substituents of appropriate geometry, such as the $-NO_2$ group, *intra*-molecular hydrogen bonding takes place (Fig. A-11).

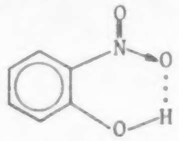


FIGURE A-11. Intramolecular hydrogen bonding with o-nitrophenol (from Ref. 1).

Since the hydrogen bonding occurs within the molecule, little external effect of it may be evident. However, when the same hydrogen bonding substituent is in the *meta* or *para* position, it cannot reach the hydroxyl of the same molecule for internal hydrogen bonding. Hence, only *inter*molecular bonding can occur (Fig. A-12). This has the effect of increasing the mutual attraction among such molecules and results in higher melting and boiling points than otherwise anticipated. *Inter*molecular hydrogen bonding may also increase the solubility in H_2O (Fig. A-13). Comparing these parameters in *o*- and *p*-nitrophenol provides a good example of this effect (see Table A-2).

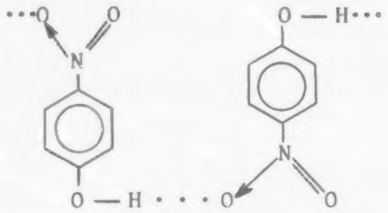


FIGURE A-12. Intermolecular hydrogen bonding with p-nitrophenol (from Ref. 1).

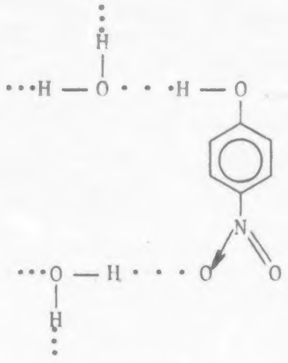


FIGURE A-13. Hydrogen bonding between p-nitrophenol and H_2O (from Ref. 1).

3.2 Acidity

The characteristic acidity of phenols is also related to the hydroxyl function (Refs. 1-4). Where ArOH represents phenols in general, acidity results from the ionic dissociation of the hydroxylic hydrogen according to the equilibrium reaction:

$$ArOH \rightleftharpoons H^+ + ArO^- \quad .$$

At a given temperature (e.g., 25°C), the concentrations of the chemical species in this equilibrium process are mathematically related according to the equation:

---

*having a permanent dipole

$$\frac{[H^+][ArO^-]}{[ArOH]} = K_a ,$$

where $[H^+]$, $[ArO^-]$ and $[ArOH]$ represent the *molar concentrations* (M) *of the respective chemical species* (in moles/liter of H_2O) and K_a is the experimentally determined acid dissociation constant for that particular compound. See Table 2 for K_a listings of various phenols.

K_a values can be used as an index of the acidity of a particular compound. For example, using the values in Table 2 for a pure, saturated solution of phenol in H_2O at 25°C, the acidity, $[H^+]$, may be determined by a simple calculation. Using the above equation with the assumption that equal amounts of H^+ and ArO^- are generated when ArOH dissociates ($[H^+] = [ArO^-]$), the equation reduces to:

$$[H^+]^2 = K_a[ArOH].$$

At saturation, the solubility of phenol in H_2O = 9.3g/100g H_2O or about 1 mole/liter (molecular weight for phenol = 94g). Thus:

$$[H^+]^2 = 1.28 \times 10^{-10}$$

$$[H^+] = (1.28 \times 10^{-10})^{1/2}$$

$$[H^+] = 1.13 \times 10^{-5} \approx 10^{-5}\ M.$$

Since pH is defined as the negative logarithm of $[H^+]$, the pH of this [illegible]tion of phenol is 5. This is acidic com[illegible] to pure H_2O which has a $[H^+] \approx 10^{-7}$ M, or [illegible].

The K_a values of most phenols fall in the 10^{-9} to 10^{-10} range. Thus, though they are acidic compared to H_2O, most phenols are weaker acids than carbonic acid, H_2CO_3 (CO_2 dissolved in H_2O), with $K_a = 4.3 \times 10^{-7}$. This characteristic is important for commercial recovery of phenols from coal and petroleum tar distillates. Strong base, i.e., high $[OH^-]$ is required to convert most phenols into their water soluble anionic form according to the equilibrium:

$$ArOH + OH^- \rightleftarrows ArO^- + HOH$$

where $$\frac{[ArO^-][HOH]}{[ArOH][OH^-]} = \frac{K_a\ (\text{phenol})}{K_a\ (\text{water})} . \qquad (\text{Eq. } 1)$$

Since K_a (water) $= 1.8 \times 10^{-16}$,

$$\frac{K_a\ (\text{phenol})}{K_a\ (\text{water})} = \frac{1.28 \times 10^{-10}}{1.8 \times 10^{-16}} = 10^6 .$$

To estimate the $[OH^-]$ necessary to maintain 99.9% of ArOH in the water soluble ArO^- form, set

$$\frac{[ArO^-]}{[ArOH]} = \frac{1000}{1}$$ and substitute in equation 1. This gives:

$$\frac{1000}{1}\,\frac{[HOH]}{[OH^-]} \approx 10^6 .$$ Rearranging,

$$[OH^-] \approx \frac{[HOH]}{1000} .$$

Since [HOH] = 55M, $[OH^-] \approx 0.05$ M. Thus, a concentration of about 0.05 moles/liter OH^- must be maintained to keep ArOH 99.9% in the ArO^- form (or pH $\geqslant$ 11.3). Strong bases (alkali) such as NaOH (lye), KOH (potash) or $Ca(OH)_2$ (slaked lime) can provide this OH concentration.

In accord with these principles, phenolics may be extracted from neutral, water-insoluble material such as petroleum or coal tar distillates by conversion to the water soluble anionic form, ArO^-, with strong base (alkali). The undissociated phenols can then be regenerated by acidification with a stronger acid such as carbonic acid (K_a 4.3×10^{-7}). By definition, a stronger acid dissociates to a greater degree and provides a greater concentration of H^+ than a weaker acid. This reconverts the ArO^- back to ArOH (see Eq. 2). Being less water soluble, the free phenolic form (ArOH) separates from solution as an oil. In the early literature, treatment with carbonic acid (CO_2 injection) was said to "spring" (free) the phenols from alkaline solution for subsequent recovery.

It should be mentioned that carboxylic acids (e.g., fatty acids) are more acidic than most phenols and carbonic acid. Hence, these acids will remain dissociated in solution after CO_2 injection. Stronger acid (e.g., mineral acids) is required to convert them to their free (undissociated) form which is water insoluble for most monoacids with more than three carbon atoms.

As electron attractive substituents are added to the benzene ring, dissociation of phenols increases, particularly at the positions *ortho* and *para* to the hydroxyl. This is evident in the K_a values of *o* and *p*-nitrophenol as compared to the K_a for *m*-nitrophenol (Table A-2). Additional *p*- and *o*-nitro groups further increase the K_a. See 2,4-dinitrophenol and 2,4,6-trinitrophenol (Table A-2). The latter is almost completely dissociated making it a strong acid (pH ∿ 1).

3.3 Chemical Reactivity

Besides forming water soluble anions in the presence of strong bases, phenols undergo a number of reactions involving hydrogen substitution on the benzene ring (Ref. 1-4). Most of these reactions proceed by attachment of a positively (+) charged or polarized chemical species at the more negatively (-) polarized of the benzene carbons, followed by loss of a H^+ from that particular benzene carbon. Presence of the phenolic hydroxyl has a strong orienting effect on the electron density of the benzene carbons, making the positions *ortho* and *para* to the hydroxyl comparatively negative and, hence, attractive to the positive entering group. Because the entering group bonds with benzenoid carbons according to their comparative electron density, this reaction is known as electrophilic substitution.

Examples of electrophilic reagents and functional groups introduced are given in Table A-3. The positive (+) polarization of the first five entering groups persists in the derived product. This has the effect of attracting electrons away from the ring carbons which reduces its tendency to react further. This "ring deactivation" in the monosubstituted product can prevent further substitution. With the last four reagents, positive polarization of the newly attached atom is negligible, hence any unsubstituted *ortho* or *para* positions remaining after initial substitution may also add the functional group to the ring. This leads to di- and trisubstituted products in the 2,4- , 2,6- and 2,4,6- positions.

TABLE A-3.

Typical Ionic Ring-Substitutions (Electrophilic) of Phenols

Reagent	Functional Group	Position
Nitric acid	$-NO_2$	*o* or *p*
Sulfuric acid (25°C)	$-SO_3H$	mostly *o*
Sulfuric acid (100°C)	$-SO_3H$	mostly *p*
Nitrous acid	-NO	*o* or *p*
Carbon Dioxide	$-CO_2H$	*o* or *p*
Alkyl halide, Alkene or Alcohol	Alkyl	*o, o, p*
Formaldehyde	$-CH_2OH$	*o, o, p*
Chlorine (H_2O)	-Cl	*o, o, p*
Bromine (H_2O)	-Br	*o, o, p*
Bromine (CS_2)	-Br	*p*

Environmental water quality is particularly concerned with the electrophilic reactivity of phenols with aqueous chlorine. Generally one of the advantages of water purification by chlorination is that, besides disinfecting the water, the chlorine oxidizes objectionable tasting or smelling organic substances into innocuous products. This is not always so with phenols. The chlorinated products can be much more distasteful (see Table B-1). This can present real problems where phenols, particularly the simple ones, exist in public drinking water which must be chlorinated to meed microbiological standards. The reaction is complex and depends on many factors including pH, chlorine concentration, and the chemical quality of the water. The principal contributor to taste and odor has been found to be 2,6-dichlorophenol, accounting for about 75% of the total odor (Ref. 7). The remainder was ascribed to 2,4-dichlorophenol and 2-chlorophenol. Increasing substitution does not necessarily intensify the effect.

Phenols also undergo non-electrophilic reactions. Generally these consist of addition of neutral, one-electron deficient fragments called "free radicals". In contrast to electrophilic substitution, the reaction is believed to proceed by initial removal (abstraction) of a hydrogen atom (H·) followed by combination of the resulting radical (ArO·) with reagent radicals. Important radical substitutions of phenols include addition by chlorine atom (Cl·) and oxidation by atmospheric oxygen. With air oxidation complex products may form, depending on the

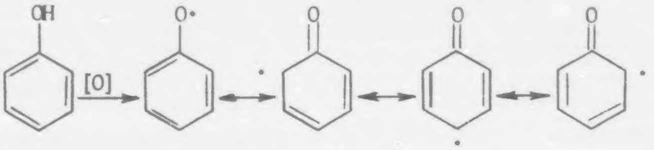


FIGURE A-14. Phenoxy radical formation.

prior substitution pattern. For example, phenoxy radicals (ArO·) may become substituents themselves at any of the dot positions indicated in Figure A-14.

Many of these oxidation products are deeply colored and their removal or alteration may be required in public water supplies. This is particularly true for water in contact with vegetation which produces significant amounts of polyphenolic polymers such as lignins and tannins.

3.4 Environmental Behavior

Although phenol and the simple substituted phenols are bactericidal in concentrations of a few percent, McKee and Wolf (Ref. 8) review studies which show that bacterial degradation of these phenols occurs in much more dilute solutions. For example, phenol was reported to disappear at the rate of 3 to 5 mg/l per day in the presence of soil and aquatic plants, 2 mg/l per day in their absence (Ref. 9). This degradation was shown to be at the expense of dissolved oxygen. Other studies (Ref. 10) indicate that complete aerobic biological dissimilation of 1 mg/l of phenol requires 1 to 7 days at 20°C, 5 to 19 days at 4°C. Anaerobic dissimilation is slower. Impoundment of water in stabilization ponds can lower the phenol content in the following manner (Ref. 11):

Day	Phenol, mg/l
0	3.6
7	0.28
14	0.20

Because of its solubility in water, phenol has been found to percolate readily through 50" of soil. Notwithstanding this potential for penetrating ground-water supplies, wells 150' from the Ohio River in W. Virginia failed to show phenols which were found in the river (Ref. 12).

4. Aquatic Sources

Aquatic phenolic wastes originate from a number of industrial operations such as coal and wood distillation, coal gasification, coke ovens, mining, oil refining and chemical plants. Phenols also enter the aquatic environment from agricultural use (sheep dip), human and animal waste, and rotting vegetation (Ref. 8).

5. Environmental Effects

Simple phenolic compounds have been described above as generally biocidal. In general, lower forms of life are more severely affected than higher forms and aquatic forms more so than terrestrial or avian. For example, in rats the oral LD$_{50}$* ranges from 78 mg/kg body weight for the potent biocide, pentachlorophenol, to 2.02 g/kg for *m*-cresol (Ref. 8). However acute or even chronic toxicity is seldom a problem with land animals. Drinking water contaminated with phenols is avoided because of the objectionable taste. Also, any phenols ingested are rapidly eliminated from the body. Poisoning of aquatic life which cannot escape such pollution is more serious.

5.1 Effects on Man

Where man is directly concerned, contamination of the aquatic environment with phenols is almost entirely an aesthetic problem (Ref. 7-10). Phenols impart such an objectionable odor and taste to water resources and food obtained from it that toxic exposure is seldom a problem. Actually this is fortunate, although it creates an economic problem in the removal of the characteristic medicinal odor and taste of phenols in water, or the rejection of phenol tainted fish flesh. A traditional means of clearing water of both toxic organisms and aesthetically displeasing organic compounds has been chlorination. However, imperceptible levels of non-chlorinated phenols can be converted to distasteful levels of chlorinated phenolic products (see section 3.3).

Drinking water standards have generally been set at a maximum of 1 μg/l of phenols in the U.S. and abroad (Ref. 8). According to ten references listed by McKee and Wolf (Ref. 8), 1 μg/l of phenols is below the taste and odor threshold, *prior* to chlorination. Threshold values ranged from 10 μg/l to 60 μg/l. Eight references list threshold values ranging from 0.1 μg/l to 20 μg/l *after* chlorination. Presumably, the spread of these values is the result of variations in experimental conditions.

A second effect of aquatic contamination by phenols is the tainting of food fish. The National Technical Advisory Committee (Ref. 10) lists examples of fish species and the concentrations of aquatic phenols which resulted in a noticeable off-flavor (Table A-4). Canning and beverage industries must also guard against contamination of their water supplies by phenolics because of their undesirable flavors or odors.

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*Lethal dose for 50% of test animals

TABLE A-4.

Concentration of Phenolic Compounds That Cause Tainting of Fish Flesh (from Ref. 10)

Compound	Concentration Affecting Taste and Odor (mg/1)
Phenol	15 to 25
Cresols	10
Xylenols	1 to 5
Pyrocatechol	2 to 5
Pyrogallol	20 to 30
α-Naphthol	0.5
Chlorophenol	0.1

5.2 Agricultural Effects

Apparently, 10 to 50 mg/1 of phenolics in livestock or irrigation water supplies endangers neither the viability nor the quality of the commodity involved (Ref. 8). However, livestock may avoid phenol tainted water.

5.3 Effects on Fish

Besides tainting fish flesh (section 5.1), phenolics are also toxic to fish. McKee and Wolf (Ref. 8) refer to a number of studies which are summarized here in terms of the median tolerance limit (TL_m) values of selected phenolic compounds. For phenol itself, Reference 1 lists TL_m values for many fish under various conditions. The TL_m's range from 5 to 56 mg/1, with most of them falling between 10 and 25 mg/1. Salmon embryos were most sensitive, mosquito fish least sensitive. Cresols showed very similar toxicity, e.g., TL_m's for salmon embryo:

Compound	24-hr TL_m (mg/1)
o-cresol	2.3
m-cresol	6.5
p-cresol	4.0

For other species most cresol TL_m's ranged between 10 and 25 mg/1, similar to the phenol TL_m's.

With the monochlorinated phenols, some species were more sensitive (e.g., bluegill), others were less sensitive (e.g., goldfish), but differences were not great. However, pentachlorophenol, used to curb bacterial slime in cooling towers, is about 100-fold more toxic than the simple phenols above. For example, the 24-hr TL_m for the sodium salt (sodium pentachlorophenate) was 0.32 to 0.35 mg/1 for fathead minnows. Other species showed very similar values.

Mononitrophenols appear to be comparable to phenol and other monosubstituted phenols discussed above. The toxicity of the isomers is in the order: $p > m > o$. When nitro and halogen substitution are combined, compounds

TABLE A-5.

Toxicity of Halogenated Nitrophenols (from Ref. 8)

Compound	LC_{100}^{a} *mg/l for 100% kill* sea lamprey larvae	LC_{10}^{a} *mg/l for 10% kill*		
		Rainbow Trout	Brown Trout	Bluegill Sunfish
2-bromo-4-nitrophenol	5	13	11	—
3-bromo-4-nitrophenol	5	11	—	15
5-chloro-2-nitrophenol	3	5	5	—
2,5-dichloro-4-nitrophenol	3	13	—	—
3,4,6-trichloro-2-nitrophenol	5	17	15	—
3-trifluoromethyl-4-nitrophenol	2	9	7	—

[a] Lethal concentration for indicated percent kill.

result which are especially toxic toward sea lamprey larvae (Table A-5). Such compounds are vital in the battle against sea lampreys in the Great Lakes.

It should be pointed out that TL_m values are parameters of mortality due to acute toxicity. As such they indicate minimum conditions for survival rather than acceptable conditions for livelihood. A more relevant criterion may be the "threshold of disturbance", the concentration which produces disturbed behavior. In this respect, phenol has an effect on trout at 1.3 mg/l, about a quarter of its TL_m (*ca.* 5 mg/l). Both threshold of disturbance and TL_m values require a certain latitude in their application to the real aquatic world because of the variations in a number of pertinent parameters such as water temperature, aeration, hardness, salinity, etc.

5.4 Effects on Other Aquatic Life

Aquatic life other than fish appear generally to be less adversely affected by phenol pollution. McKee and Wolf (Ref. 8) list numerous reports of the effect of phenol on biota. Some of this data appears in Table A-6. Both threshold and acute toxic effects tend to occur at higher phenol concentrations for these random biota than for fish. Threshold concentrations for noticeable effects on four selected biota by various phenols are given in Table A-7. A number of substituted phenols have more potent effects than phenol itself.

Pentachlorophenol (Fig. A-4), either free ("Penta") or in its water soluble salt form ("Santobrite"), is one of the most potent, broadly toxic phenols. It is widely employed for a number of biocidal and biostatic applications, e.g., bacterial slime and algae control in cooling towers or wood preservative for telephone poles, railroad ties and dock pilings. As with fish (section 5.3), pentachlorophenol is more toxic than most phenols toward aquatic biota in general, probably by a factor of 10 or more. Extreme water insolubility of the free acid form is the only protection afforded to aquatic life in water in direct contact with acid treated surfaces. McKee and Wolf (Ref.8) discuss numerous examples involving the salt form.

TABLE A-6.

Effects of Phenol on Lower Aquatic Life (from Ref. 8)

Concentration in mg/l	Organism	Effect
1	*Platymonas*	Limits photosynthesis
3	*Mytilias edulis*	Threshold effect
5	*Daphnia* (young)	" "
8-10	*Daphnia magna*	Lethal
14	*Daphnia* (adult)	Threshold effect
15	Tubeworm	" "
15	Isopod	" "
16	*Daphnia*	" "
25	*Gammaridae*	Lethal
30	*Microregma*	Threshold effect
40	*Scenedesmus*	" "
40-50	*Culex* larvae	" "
50	Isopod	" "
50-60	*Daphnia*	" "
94	*Daphnia magna*	Immobilization
94-100	Snail	Toxic effect
100-120	*Pionocypris*	Threshold effect
108	*Diaptomus oregonensis*	" "
122	*Cyclops vernalis*	" "
150-180	*Cyclops* and *Sayomia* larvae	" "
200	*Tubifex*	Toxic effect
200	Crustacea	" "
200	Molluses	" "
251-261	*Navicula*	" "
800-1000	*Culex* pupae	Threshold effect
1000	Protozoa	Toxic effect
1000	Rotifers	" "
1600	Bacteria	" "

TABLE A-7.

Concentrations for Threshold Effects in Selected Biota (from Ref. 8)

Phenolic Compound	Threshold Concentration in mg/l for			
	Daphnia (a crustacean) (23°C)	*Scenedesmus* (an alga) (24°C)	*Microregma* (a protozoan)	*E. coli* (a bacterium) (27°C)
Phenol	16	40	30	>1000
p-Aminophenol	0.6	6	2	8-10
p-Butylphenol	8	10	10	> 100
o-Cresol	16	40	50	600
m-Cresol	28	40	20	600
p-Cresol	12	6	10	>1000
o-Nitrophenol	60	36	40	>1000
m-Nitrophenol	24	28	20	300
p-Nitrophenol	14	72	20	100
2,4-Dinitrophenol	6	40	—	> 100
Dinitro-o-cresol	8	36	30	100
o-Xylenol	16	40	10	500
m-Xylenol	24	40	70	> 100
p-Xylenol	10	40	50	> 100
Resorcinol	0.8	60	40	>1000
Hydroquinone	0.6	4	2	50
Pyrocatechol	4	6	6	90
Pyrogallol	18	8	50	30

6. Standards and Criteria

Standards for dissolved phenols in water for human consumption are more stringent than other uses because of the tainted flavor imparted by traces (mg/l) of phenols. U.S. Public Health Standards (Ref. 9) recommend a maximum of 1 μg/l. This level is endorsed by McKee and Wolf (Ref. 8) and the first National Technical Advisory Committee on Water Quality Criteria (Ref. 10). The latter also recommended complete absence of phenols in public water supplies.

For non-human uses, McKee and Wolf (Ref. 8) suggest the following maximum permissible concentrations (MPC):

irrigation	50 mg/l ,
livestock water	1 g/l
aquatic biota	0.2 mg/l .

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10. Water Quality Criteria, Report of the National Technical Advisory Committee to the Secretary of the Interior, U.S. Government Printing Office, Washington, DC 20402 (1968).

B. ANALYSIS

Phenols occur in waste effluents from petroleum and coal processing and chemical manufacturing. Most of these phenols impart an undesirable taste or odor to drinking water at the 10 to 100 μg/l level. Presence of phenols in public water supplies is further complicated by marginal chlorination which can produce the even more objectionable chloro derivatives. Some of these are detectable by taste or odor at only a few μg/l (Table B-1). Thus, monitoring phenols is important in water used for drinking. This requires sensitive (μg/l), reasonably selective analytical methods.

TABLE B-1.

Threshold Concentrations of Chlorinated Phenols (from Ref. 1)

Phenolic Compound	μg/l	
	Taste	Odor
o-Chloro	2	2
p-Chloro	1000	250
2,4-Dichloro	8	2
2,6-Dichloro	2	3

Standard methods for the analysis of aquatic phenols are described in several references:

Standard Methods for the Examination of Water and Waste Water, 13th Ed., 1971 (Ref. 2);

Annual Book of ASTM Standards, Part 23, 1973 (Ref. 3);

Methods for Chemical Analysis of Water and Wastes, 1974 (Ref. 4);

Methods for Analysis of Organic Substances in Water, 1972 (Ref. 5).

Two general procedures are recognized (Ref. 2-5):

a) Reaction with 4-aminoantipyrine (4-AAP) to form a characteristic dye which can be determined colorimetrically;

b) Gas chromatography (GC) directly on the water sample.

Extensive analytical details are presented in References 2 and 3, including procedural modifications according to the nature of the sample. These are the primary references; the methods in References 4 and 5 are adaptations for U.S. Environmental Protection Agency (EPA) and U.S. Geological Survey (USGS) use. More frequent updating is possible with the ASTM manual (Ref. 3), otherwise Standard Methods (Ref. 2) has virtually identical procedures.

A colorimetric alternative to the 4-AAP method has been proposed (Ref. 6, 7) using the reagent 3-methyl-2-benzothiazolinone hydrazone (MBTH). A fourth general method involves measurement of ultraviolet (UV) absorbance according to pH (Ref. 8, 9). These two methods have not yet been endorsed by the EPA or the sponsors of either Standard Methods (Ref. 2) or the ASTM (Ref. 3); both may offer some advantages over existing official methods. This is discussed below.

A fifth method suggested by Kawahara (Ref. 10, 11) is based on (a) separation of the weakly acidic organic fraction from the aqueous sample, (b) reaction to form the pentafluorobenzyl ether, followed by (c) GC analysis with electron capture detection (ECD). Sixth, Argauer has prepared chloroacetate esters of phenols directly from aqueous samples for analysis by ECD-GC (Ref. 12). Seventh, UV fluorescence spectroscopy has been applied to the determination of phenol standards in water (Ref. 13).

Each of the above methods has limitations, some of which could be surmounted with more sophisticated analytical instrumentation such as combined gas chromatography-mass spectrometry (GC-MS). Most EPA regional technical support laboratories now have computerized GC-MS instrumentation. If circumstances warranted, phenols could be monitored from aquatic grab samples with this equipment.

1. Sampling

Recommended procedures for sampling aquatic phenols are given in:

a) Standard Methods (Ref. 2), Section 200A;

b) ASTM Annual (Ref. 3), Sections D 510, D 1192 and D 1496;

c) USGS Methods (Ref. 5), Part 1.

The ASTM Annual contains the most extensive details. Generally, samples should be representative and collected in clean, inert containers. Glass bottles, 1-liter capacity, sealed with Teflon lined screw caps are acceptable (Ref. 5). Prior to use they should have been thoroughly washed in hot detergent, rinsed with warm tapwater, dilute hydrochloric acid (HCl) and distilled water, then dried overnight at 300°C (Ref. 5). The Teflon liners should be soaked first in dilute HCl, then in redistilled acetone. Although the ASTM currently permits the use of polyethylene bottles, both the USGS (Ref. 5) and the EPA (Ref. 14) advise against them. Polyethylene may leach organic impurities and absorb phenolics.

1.1 Sample Preservation

Phenols are susceptible to oxidative degradation by chemical or biological means at the concentrtions (< 1 mg/l) usually found in water (Ref. 2, 3). If analysis is delayed more than 4 hours after sample collection, the samples should be preserved by acidification to pH 4 with phosphoric acid, followed by addition of copper sulfate and storage at 5 to 10°C. The acid suppresses formation of the phenolate anion (ArO^-) and cupric hydroxide ($Cu(OH)_2$), both of which facilitate chemical oxidation of phenols. Dissolved cupric ion (Cu^{+2}) inhibits microbial degradation of phenols.

If the sample originally had the odor of chlorine, or if the acidified sample liberates iodine when potassium iodide is added, an oxidant is present which must be reduced at once (Ref. 2, 3). Addition of ferrous sulfate or sodium arsenite is recommended. If hydrogen sulfide or sulfur dioxide was liberated upon acidification, it should be removed by aeration prior to adding copper sulfate.

1.2 Sample Preparation

One 4-AAP method (section 2) and one UV absorption method (section 5.2.2) require that phenols be distilled to remove interfering substances (Ref. 2-5). Prior acidification (section 1.1) maintains the phenols in their undissociated or free form, assuring distillation of phenols which are sufficiently volatile. Under alkaline conditions (pH $\geq$ 12) the dissociated form (phenolate anion) is not distilled. Certain phenols (e.g., *m*- and *p*-chlorophenols, *m*- and *p*-nitrophenols) do not distill efficiently under the experimental conditions (see Table A-2).

If the aqueous distillate is turbid or if the original sample was oily, organic solvent extraction under alkaline conditions may be advisable to remove organic interferences. The pH is adjusted to $\geq$ 12 with alkali to convert the phenols to their phenolate anion forms which are soluble in water but not in organic solvents (see section 3.2, Part A). This allows neutral and basic organic substances to be extracted from the sample with organic solvents such as chloroform, ether or carbon tetrachloride while the phenolates remain dissolved in the aqueous phase. Subsequent acidification to pH 4 regenerates the free phenols for the distillation step. Addition of alkali must be performed either prior to copper sulfate addition or after an initial distillation, otherwise cupric hydroxide will form which promotes oxidation of phenols.

Some methods require extraction of the phenols from the acidified sample into organic solvent (see sections 2, 3, and 6). Most remaining organic interferences can be eliminated by fractionating the organics into (a) strong acids, (b) weak acids and (c) neutrals and bases. The weak acid fraction contains most phenols; see sections 3.9 and 6.1 for details.

2. 4-Aminoantipyrine (4-AAP) Method

Many phenols react with the organic chemical, 4-aminoantipyrine in the presence of potassium ferricyanide at pH 10 to form a reddish-brown dye (Ref. 2-5). This dye can be measured directly with a spectrophotometer at phenol concentrations of 1 to 50 mg/l. Below this level the dye is concentrated by extraction into 25 or 50 ml of chloroform from a 500 to 1000 ml water sample. Absorbance of light by the dye is measured at 510 nm in the direct method or at 460 nm with the chloroform extract. Calibration with freshly prepared standard phenol solutions and blanks is necessary. Ultimate sensitivity of the chloroform extraction method is about 1 μg/l phenol in water.

Technicon (Ref. 15, 16) has automated the direct 4-AAP reaction method with phenol distillates. Figure B-1 shows the details schematically. Water samples or phenol standards introduced at A are preheated to 130°C and proceed to B where the volatile phenols are distilled into the trap D. Here, reagents from C react with most volatile phenols to form the characteristic 4-AAP/phenol dye. The absorbance of light by the dye at 505 nm is measured in a 50 mm cell at E. About 40 samples or standards can be analyzed per hour at sensitivities comparable to the manual method.

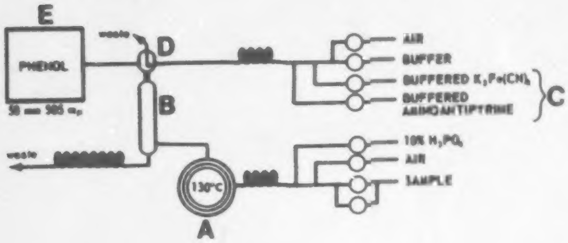


FIGURE B-1. Schematic diagram of automatic phenol analysis of surface water samples by the 4-AAP method (from Ref. 15).

Two refinements of the original Technicon 4-AAP procedure are now available for the Autoanalyzer. One is a minor modification (Appendix I) recently developed by the EPA Methods Development and Quality Assurance Research Laboratory at Cincinnati, Ohio (Ref. 17). This EPA method entitled "Phenolics, Automated 4-AAP Method with Distillation" is included in the most recent edition of Ref. 4 (1974). Revised schematic diagrams for the Autoanalyzer manifolding and sample train are included along with preliminary precision and accuracy data (see Appendix I).

A significantly different automated 4-AAP procedure has been published recently by the Canadian Department of the Environment (Ref. 7). Except for the 4-AAP dye reagent, most of the other reagents differ from those used in the other 4-AAP methods (Ref. 2-5, 15, 16). For example, sulfuric acid is employed instead of phosphoric acid, potassium hydroxide is used instead of sodium hydroxide, and potassium persulfate is used as an oxidant instead of potassium ferricyanide. As with the EPA automated procedure (Appendix I), the phenols are distilled prior to reaction with 4-AAP; however, in the Canadian automated procedure (Ref. 7) the 4-AAP-phenol dye is also extracted into chloroform before colorimetry. Such differences in procedure have necessitated modifications of the Autoanalyzer apparatus, as described in Reference 7. Analytical precision is also discussed there and compared to the alternative MBTH method (see section 4.3).

2.1 Limitations

Since light absorbance by the 4-AAP-phenol dye varies according to the phenol structure, precise calibration of this method for a mixture of phenols is not possible without knowing which phenols are present and what their ratios are. Phenol itself is taken as the standard and analytical results are reported on this basis.

Not all phenols react with 4-AAP to form the dye. Examples include phenols with the following *para* substituents (Ref. 2):

alkyl (methyl, ethyl),
aryl (phenyl),
benzoyl,
formyl (aldehyde),
nitro,
nitroso.

On the other hand loss of the following *para* substituents under the reaction conditions may permit the reaction with 4-AAP to form the dye (Ref. 3):

carboxyl,
halogen,
methoxyl,
sulfonate.

2.2 Modification for *Para* Halogens

To overcome some of the above limitations, Standard Methods, 13th Ed. (Ref. 2) offers a tentative method for halogenated phenols, particularly for those substituted in the *para* position. Instead of steam distillation to remove interferences, the phenols are extracted from the acidified aqueous sample with a water-insoluble organic solvent. This solvent extract is then shaken with aqueous ammonia to convert the phenols to their water-soluble, solvent-insoluble phenolate form and extract them from the organic solvent phase into the aqueous phase. Standard Methods recommends petroleum ether as the organic solvent; however, this has been criticized as inadequate to extract many halogenated phenols (Ref. 18). Chloroform has been suggested as a better solvent. Probably methylene chloride or ether would also suffice.

Few interfering substances can accompany phenols through these steps. The pH of the ammoniacal extract is then adjusted to 7.9 with phosphate buffer and treated with 4-AAP and potassium ferricyanide to form the dye.

Pentochloro- and pentabromophenol do not form the dye under these conditions.

For this modified method 2,4-dichlorophenol is used as the calibrating compound. Light absorbance is measured at 500 nm. Reference 1 lists (a) absorptivity values of the dye complex from 16 halogenated phenols and (b) typical analytical standard deviations based on the standard, 2,4-dichlorophenol.

3. Direct Gas Chromatography

Water samples containing 1 mg/l or more of phenols may be analyzed by direct injection into a gas chromatograph equipped with a flame ionization detector (FID). Extensive analytical details are given in both Standard Methods (Ref. 2) and the ASTM Annual (Ref. 3). Since 1 mg/l of phenols represents a rather substantial pollution level for phenols, this analytical method applies mainly to waste waters and sample concentrates.

The GC sample size (3 to 5 μl) requires that the FID be able to detect and measure nanograms of phenols. Ordinarily this is no problem with samples of pure phenols in clean water. However, waste water samples may pose specific difficulties which must be dealt with according to the nature of the sample.

3.1 General GC Aspects

Some basic essentials of GC are discussed in this volume under pesticides, and oil and grease. The reader is referred to:

a) Pesticides, Part B (H2O-PES, Methods), Sections 7.1 and 7.4;

b) Oil and Grease, Part B (H2O-OIL, Identification), Section 1.1.

Standard Methods (Ref. 2) and the ASTM Annual (Ref. 3) contain detailed specific GC instructions.

Like pesticides, phenols are analyzed on relatively short (1.5 to 3 m), packed GC columns under isothermal conditions in 30 to 45 min. Phenols, being less sensitive than pesticides to decomposition on heated metal surfaces, may be analyzed with stainless steel GC columns.

As in GC analysis of oils, direct GC analysis of phenols utilizes the FID. This detector is insensitive to the passage of mg quantities of hot water vapor (steam) from the sample. However, the rest of the sample train may be affected. For example, the water may "steam clean" the GC sample train, liberating interfering substances ("ghosts") which would otherwise remain immobile within the GC system. Obviously, the GC partitioning liquid phase used must be chemically insensitive to these repeated bursts of steam or other substances in the sample.

3.2 GC Sample Preparation

To avoid chemical or biological degradation, samples should be analyzed as soon as possible. Until then, they should be refrigerated and protected from atmospheric oxygen (Ref. 2). If the samples are alkaline, they should be acidified slightly. This averts phenol sample losses in the non-volatile phenolate form (Table B-2). Copper sulfate has not been specifically recommended as a sample preservative for this GC method.

TABLE B-2.

Effect of pH in GC Analyses of 2,4-Dichlorophenol (from Ref. 2)

pH	4.5	7.7	9.7	10.8	11.7
Peak area (sq. in.)	2.88	2.90	2.90	2.93	1.08

The usual phenol preservatives, phosphoric acid and copper sulfate, are hardly the sort of substances to be desired within the GC sample train. The effects of such unwanted accumulations can be minimized by using disposable pyrex injection-port inserts. These are generally available from GC manufacturers. They are also useful in trapping tarry or solid material in the sample.

Particulate or suspended matter, unless extremely fine, can plug the injection microsyringe. Centrifugation or filtration is recommended so long as phenols are not also removed. Otherwise, a colloid mill is suggested to homogenize the sample. Sometimes these troublesome solids dissolve upon acidification (Ref. 3).

3.3 GC Apparatus

A gas chromatograph equipped with an FID and a column oven capable of isothermal operation to 210°C ± 0.2 is recommended (Ref. 2, 3). Temperature programming may be useful in the future but is not presently required. Gas chromatograms are recorded on a 1-mv strip-chart recorder with a response time ≤ 1 sec.

Three GC column options are offered (Ref. 2, 3):

No. 1. Carbowax 20M-TPA. A 3-mm × 3-m (1/8 in. × 10 ft) stainless steel column packed with 60/80 mesh, flux-calcined diatomite (acid-washed, silanized) coated with 20% terephthalate-terminated Carbowax 20M.

No. 2. FFAP, 1.5 m. A 3-mm × 1.5-m (1/8 in. × 5 ft) stainless steel column packed with 70/80 mesh, flux-calcined diatomite (acid-washed) coated with 5% FFAP (nitroterephthalate-terminated Carbowax 20M).

No. 3. FFAP, 3 m. A 3-mm × 3-m (1/8 in. × 10 ft) stainless steel column packed with 60/80 mesh fluorocarbon resin coated with 10% FFAP.

3.4 GC Operations

New GC columns should be conditioned for a day prior to use by heating at 30 to 50°C above the analysis temperature under a carrier gas flow of 20 to 40 ml/min (Ref. 2, 3). During the conditioning phase the effluent end of the column should remain disconnected from the detector. Occasional injection of 3 to 5 µl of water facilitates column conditioning. Water injection is also recommended procedure after each GC run (chromatogram) in order to clear the GC sample train (injection port, column and detector) of residual sample and artifacts ("ghosts") which would interfere with the analysis of the next sample.

Calibration of the instrument is accomplished by injecting freshly prepared solutions of phenol standards. GC relative retention time (RR_t) of the twelve phenol standards are given in Table B-3 (RR_t for phenol = 1.0). Detector calibration factors for these phenols are given in units of nanograms of standard per square inch of GC peak area (ng/in.^{2}).

Typical operating conditions of the gas chromatograph for column No. 1, 3 and 3 are given in Table B-4. These conditions apply to chromatography of both the calibration standards and the analytical samples. Before

TABLE B-3.

Chromatographic Retention Times (from Ref. 2)

Phenolic Compound	Boiling Point	Column No. 1		Column No. 3	
		Relative Retention	ng per sq in.	Relative Retention	ng per sq in.
Phenol	182 C	1.0	45.2	1.0	28.8
o-Cresol	192 C	1.0	51.0	1.0	27.0
m-Cresol	203 C	1.3	51.9	1.3	30.5
p-Cresol	202 C	1.3	51.3	1.3	31.3
o-Chlorophenol	176 C	0.8	86.7	0.6	44.8
m-Chlorophenol	214 C	3.6	106	3.6	45.4
p-Chlorophenol	217 C	3.6	125	3.6	46.5
2,3-Dichlorophenol	—	1.8	76.5	1.9	46.8
2,4-Dichlorophenol	210 C	1.8	117	1.9	55.3
2,5-Dichlorophenol	210 C	1.8	113	1.9	50.4
2,6-Dichlorophenol	220 C	1.6	71.5	1.5	50.0
3,4-Dichlorophenol	254 C	—	—	11.5	43.0

TABLE B-4.

Typical Operating Conditions for Chromatographic Column (from Ref. 2)

Column and Packing	Column No. 1	Column No. 2	Column No. 3
Carrier gas	Helium	Helium	Nitrogen
Carrier gas flow, ml/min	25	35	60
Temperature, degrees Centigrade:			
Injection port	250	205	250
Column	210	147	188
Hydrogen for detector, ml/min	25	25	30
Chart speed, in./hr	12	12	12
Sensitivity, mV	1	1	1
Electrometer range	1	0.1	1
Attenuation	1	1	1
Sample volume, microliters	1	1	1

sample analysis, the GC system should perform reproducibly with the standards (Ref. 2, 3). Replicate RR_t's must agree within two significant figures. Peak areas of calibrated amounts of a standard should agree within ±1% on three consecutive injections. Best results are obtained when the GC peak rises to about 50% of full scale on the recorder.

3.5 Phenol Identification

Identification of a phenol in an analytical sample is based upon close agreement of its relative retention time (RR_t) with the RR_t of one of the standards. More than one compound in the sample, not necessarily a phenol, may be detected at the same RR_t on a single GC column under the conditions of the analysis. This ambiguity may be reduced by performing a second gas chromatogram on a different GC column under different conditions, but confirmatory techniques may be necessary. This involves trapping the sample component(s) before they pass through the FID and identifying them by infrared (IR), ultraviolet (UV) or mass spectroscopy.

Detailed instructions for determining RR_t's are given (Ref. 2, 3). The RR_t for a particular standard is taken as the average of three analyses. Values listed in Table B-3 are for guidance only. The only valid RR_t's are those determined experimentally under actual analytical conditions used for unknown samples.

3.6 Phenol Quantitation

Measurement of the amount of a particular phenol depends upon the experimentally determined detector response factor (calibration factor) for that compound (Ref. 2, 3). The factors in Table B-3 are for guidance only. Before any calibration factor can be accepted, three consecutive experimental determinations must agree to within ±1%. Since this is the limit of readability of the microsyringe, operator skill and care is required. Calibration factors are determined from the peak area in one of the following ways:

a) triangulation, i.e., conversion of the Gaussian GC peak area to a triangle approximation, 1/2 width × height;

b) mechanical or electronic signal integration;

c) weighing of recorder paper cutouts of the GC peaks.

3.7 Gas Chromatograms

The same example gas chromatograms are presented in Reference 2 and 3. Figure B-2 (a, b) shows chromatograms of ten phenol standards taken on column No. 1 under conditions similar to those in Table B-4. Figure B-4 (a, b) shows these standards similarly chromatographed on column No. 3. Figure B-3 corresponds to five standards chromatographed

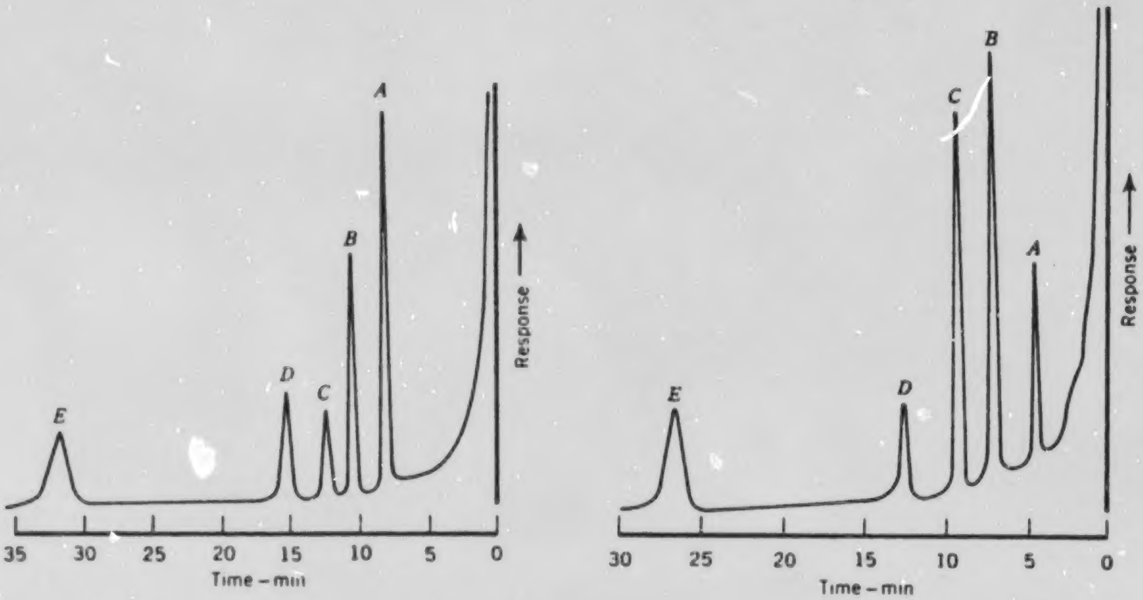


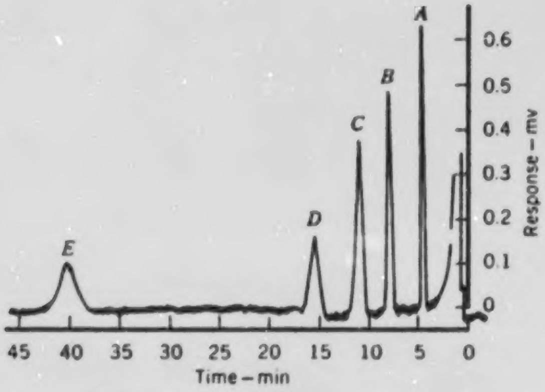
FIGURE B-2(a).

A = *o*-chlorophenol
B = phenol
C = *m*-cresol
D = 2,4-dichlorophenol
E = *p*-chlorophenol

FIGURE B-2(b).

A = *o*-cresol
B = *p*-cresol
C = 2,6-dichlorophenol
D = 2,3-dichlorophenol
E = *m*-chlorophenol

FIGURE B-2. Chromatogram of phenol standards on GC column No. 1 (from Ref. 3). GC conditions as per Table B-4, except helium flow = 20 ml/min.



A = *o*-chlorophenol
B = phenol
C = *m*-cresol
D = 2,4-dichlorophenol
E = *p*-chlorophenol

FIGURE B-3. Chromatogram of phenol standards on GC column No. 2 (from Ref. 3). GC conditions as per Table B-4.

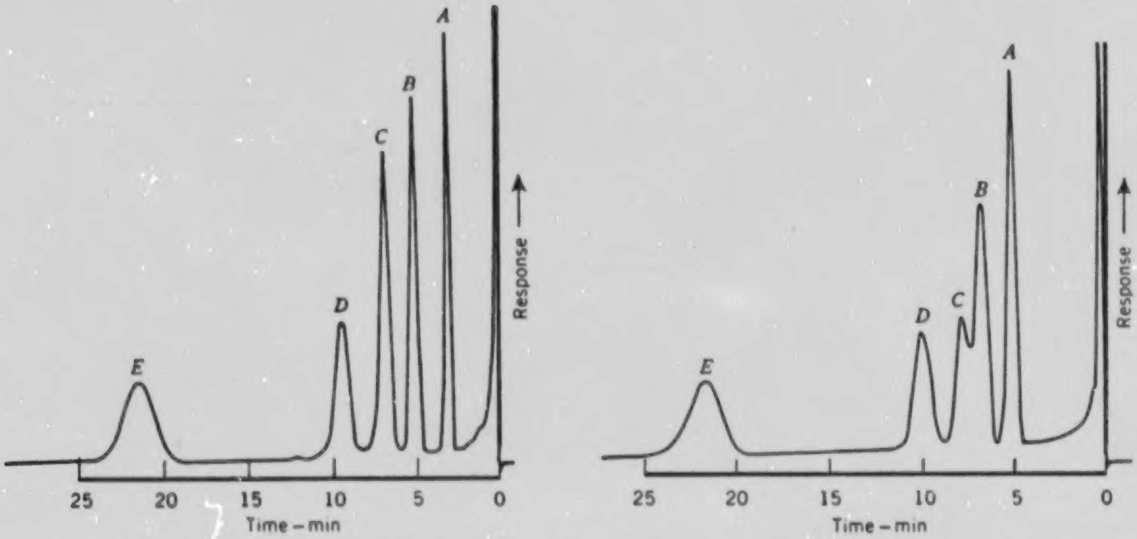


FIGURE B-4(a).

A = *o*-chlorophenol
B = *p*-phenol
C = *m*-cresol
D = 2,4-dichlorophenol
E = *p*-chlorophenol

FIGURE B-4(b).

A = *o*-cresol
B = *p*-cresol
C = 2,6-dichlorophenol
D = 2,3-dichlorophenol
E = *m*-chlorophenol

FIGURE B-4. Chromatogram of phenol standards on GC column No. 3 (from Ref. 3). GC conditions as per Table B-4.

on column No. 2. Both references inexactly refer to the liquid phases as polyester. There are many kinds of polyesters used in gas chromatography. The phases used here are more properly considered ester terminated polyethers. Both are made from the polyether, Carbowax 20M. One is terephthalate terminated, the other is nitroterephthalate terminated.

3.8 Analytical Results

Each compound reported is characterized in terms of its retention time, i.e., the time lapse between sample injection and emergence of the peak top. This is divided by the retention time of phenol to obtain a relative retention time (RR_t). Using the experimentally determined calibration factor of the standard, the concentration of a sample compound is calculated as:

$$ng/l = \frac{A \times B}{C} ,$$

where A = sample compound peak area (in.^{2}),
B = calibration factor of standard with corresponding retention time (ng/in.^{2}),
C = GC sample volume (μl).

For peaks containing more than one phenol, a weighted average calibration factor may be employed, if the ratios of phenols within the peak can be determined. Otherwise, the concentration may be reported as a single assumed constituent.

The solutions in Table B-5 were employed to determine the precision possible with this GC method (Ref. 3). The results were as follows:

TABLE B-5.

Precision Testing Solutions (from Ref. 3)

Phenolic Compounds	Master Solution (mg/liter)			
	1	2	3	4
Phenol	20	80	40	10
m-Cresol	40	10	20	80
o-Chlorophenol	10	20	80	40
2,4-Dichlorophenol	80	40	10	20

Phenol: $S_T = 0.048X + 0.6$
$S_O = 0.017X + 0.3$
m-Cresol: $S_T = 0.029X + 2.2$
$S_O = 0.014X + 0.7$
o-Chlorophenol: $S_T = 0.083X + 1.2$
$S_O = 0.031X + 0.2$
2,4-Dichlorophenol: $S_T = 0.172X + 0.1$
$S_O = 0.036X + 1.2$

where: S_T = overall precision in mg/liter,
S_O = single-operator precision in mg/liter, and
X = concentration of phenolic determined in mg/liter.

Baker (Ref. 19) has compared the accuracy of this method with that of the 4-AAP method. The results, shown in Table B-6, suggest that greater accuracy is obtainable from the GC method at mg/l concentrations. A major factor is the capability of calibrating the individual contributions of the phenolic compounds found in the gas chromatogram. In the 4-AAP method, calibration is based on a single compound, such as phenol or 2,4-dichlorophenol.

3.9 Advantages and Limitations

Where there is a sufficient quantity of an individual phenolic compound (e.g., 1 mg in a 1-liter sample), the direct GC method offers the prospect of tentatively identifying and measuring several phenols in a single analysis. Precision and accuracy appear to be reasonable in the absence of organic interferences. Calibration according to individual phenolic constituents is feasible with this method; whereas, it is impractical with the 4-AAP method unless some auxiliary technique such as the GC method is employed.

TABLE B-6.

Comparison of Phenolic Analytical Procedures (from Ref. 3)

Phenolic Compound	Concentration, mg/liter		
	By Weight	4-Amino-anti-pyrine	G C
Phenol	1.06	0.97	0.97
o-Cresol	1.04	0.64	1.03
m-Cresol	1.02	0.38	1.03
p-Cresol	1.00	0.00	1.00
			3.94
Composite	4.12	2.40	4.11

Limitations of the direct GC method depend on the nature of the sample. If the sample contains mg/l of phenolic compounds in otherwise relatively clean water, this method appears to be the simplest and most accurate of the two approved methods. Gas chromatography on a dual column isothermal instrument equipped with two independent detectors (FIDs) and recorders could be arranged to handle about twenty such analyses per day with minimal operator intervention. If more than twenty samples per day were to be analyzed, programmed automatic sample analysis on several GC instruments is still within the supervisory capacity of a single operator.

Organic compounds in the sample which have retention times similar to those of the phenol standards can interfere seriously with this method. Maintaining the sample in a neutral or slightly acidic condition (pH ≤ 7) suppresses the appearance of organic bases (amines) in the chromatogram. Interfering carboxylic acids can be separated from all but the most acidic phenols by saturating the original slightly acid solution with $NaHCO_3$ (pH 7.5 to 8.0) and extracting with an immiscible organic solvent. Most phenolics enter the organic phase, while most carboxylics remain in the aqueous (bicarbonate) phase. Separation of the phenolics from the neutrals involves conversion of the phenols into the water soluble phenolate form with alkali (base) (see Part A, section 3.2). Neutral organics can then be extracted with a water immiscible organic solvent. Reacidifying the alkaline solution regenerates the free phenols which are recovered by extracting again with a water immiscible organic solvent.

Sample cleanup should be restricted to the minimum necessary to obtain meaningful gas chromatograms. Since the FID generally responds to all organic carbon below the oxidation state of CO, detection of an organic compound at the relative retention time (RR_t) of a phenol standard does not assure its identification as a phenol on any particular GC column. A check of the RR_t on a different GC column helps confirm the identity but IR, UV and/or mass spectroscopic analysis of collected GC fractions is more rigorous.

4. Automated 3-Methyl-2-Benzothiazolinone Hydrazone (MBTH) Method

If the 4-AAP method is to be replaced by a superior colorimetric method, the most likely alternative at the present time is the oxidative coupling reaction of phenols with MBTH reagent. Two MBTH procedures have been developed for automated analysis of phenols (Ref. 6, 7).

4.1 Chemistry

The chemical oxidation and coupling reaction is considered to take place primarily at the *para* position of the phenol as in Equation 1 (Ref. 6). If the *para* position is blocked with an unremovable functional group, the MBTH reagent can couple at an unoccupied *ortho* position.

Friestad et al. (Ref. 6) have studied the MBTH method with 32 different phenolic compounds, including 20 phenolics bearing a *para* substituent (see Table I, Reference 6). Seven *para* substituted phenols which failed to produce the dye with the 4-AAP method gave a partial response to the MBTH method. Two *para* substituted phenols (2,4-dinitrophenol and 2,6-diiodo-4-cyanophenol) failed to respond to either the 4-AAP or the MBTH method.

Extensive descriptions of many aspects of the automated analysis with MBTH reagent are presented in References 6 and 7 including Autoanalyzer sample train schematics for each procedure.

4.2 Detection Limits and Precision

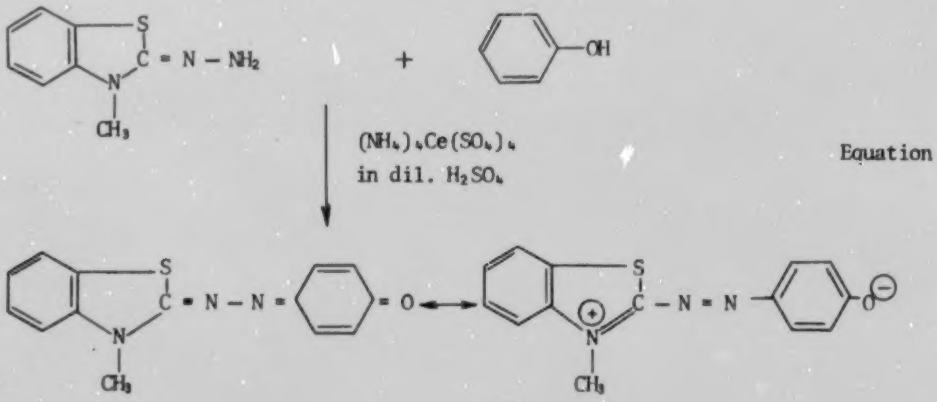
The lower limit of detection for automatically distilled samples with the first method (Ref. 6) was:

a) about 10 μg/l for phenol;

b) better than 100 μg/l for most of the other phenols in Table I, Reference 6.

Ten analyses at 150 μg/l had a relative standard deviation of 7.6%.

In the Canadian study, Goulden et al (Ref. 7) essentially followed the earlier procedure in Reference 6. However, the new procedure also features extraction of the MBTH-phenol dye into chloroform for colorimetry (as does their 4-AAP procedure). The limit of detection for the analysis of phenol was 0.2 μg/l



Equation 1.

with the new MBTH method (Ref. 7). For 11 replicate determinations of phenol at 5 μg/l the relative standard deviation was 2.4% for the new MBTH method.

4.3 Comparison of the MBTH and 4-AAP Methods

Goulden et al. (Ref. 7) compared their MBTH method with their 4-AAP method. The same modified Autoanalyzer apparatus was used for both. Each method gave the same limit of detection, 0.2 μg/l, for phenol. At 5 μg/l phenol concentration relative standard deviation was somewhat better with the MBTH method: 2.4% vs. 3.6% for the 4-AAP method.

4.4 Advantages and Limitations

The MBTH method responds, at least partially, to some *para* substituted phenols which do not react at all with the 4-AAP method (see section 2.1). Examples include phenolics with the following *para* substituents (from Reference 6, Table I):

cyclohexyl,
amino,
hydroxyl,
nitro,
phenyl.

The MBTH method has also been reported to be more reliable than the 4-AAP method at the 5 μg/l level (Ref. 7).

Several types of organic compounds have been conceded to interfere with the MBTH method (Ref. 6). Examples include:

aldehydes,
ketones,
carbazoles,
stilbenes,
azo dyes,
imines,
aryl amines.

5. UV Absorbance According to pH

A phenol or a mixture of phenols may be determined in water samples by measuring the difference in absorption of UV light as the pH is changed from slightly acid (pH 5) to strongly alkaline (pH 12) (Ref. 8, 9). Most phenols are weak acids so that the predominant form at pH 5 is the undissociated, free acid form. Exceptions include the strong acids 2,4-dinitrophenol, 2,4,6-trinitrophenol (picric acid) -- see discussion in Part A, section 3.2. At pH 12 both strongly and weakly acidic phenols exist predominantly in their dissociated phenolate anion form. Figure B-5 shows similar spectra for both forms of phenol.

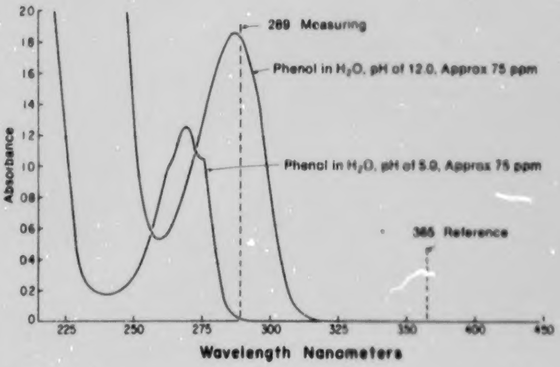


FIGURE B-5. *Phenol UV absorption in acidic and basic water solutions (from Ref. 8).*

The spectrum for the phenolate anion is displaced toward longer wavelengths (λ) at pH 12 compared to the free phenol. This displacement of the absorption maximum (λ_{max}) to longer wavelengths is known as the "bathochromic" shift. Figure B-5 also indicates that UV absorption at λ_{max} is greater for the phenolate anion (pH 12) than for the free phenol (pH 5). Substituted phenols behave similarly. This variation in the UV absorbance with pH is the basis for the spectrophotometric determination of phenols in the presence of other UV absorbing substances.

A specially constructed UV spectrophotometer measures absorption at a fixed measuring wavelength (λ_{meas}) corresponding to high absorption for the base form and low absorption for the acid form (Ref. 8, 9). In Figure B-5 the measuring wavelength is λ_{meas} = 289 nm, a convenient line in the mercury vapor spectrum. The absorption is recorded first at pH 5 and then at pH 12. The difference in absorption is due to the conversion of the free phenol to the phenolate anion. Absorbances are measured differentially with respect to a reference wavelength, λ_{ref} = 365 nm, where neither the acid or the base form absorbs significantly. This helps to compensate for

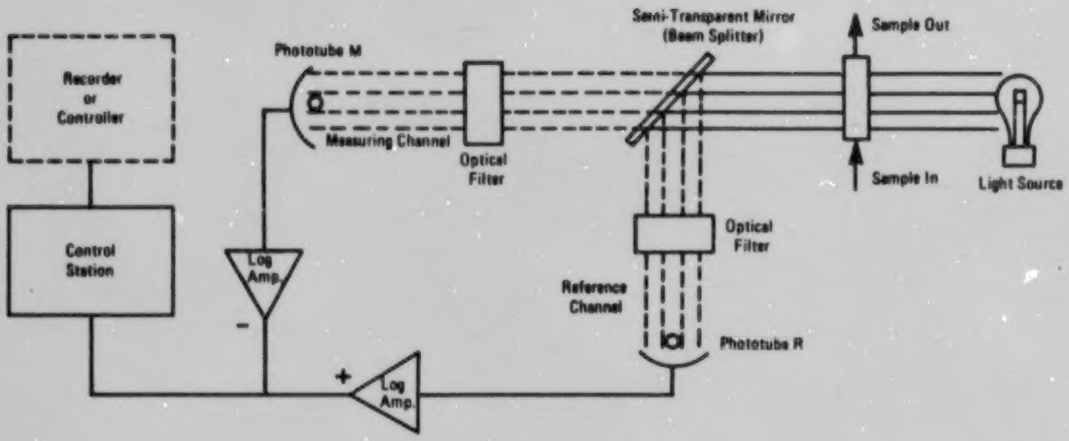


FIGURE B-6. DuPont model 400 Photometric Analyzer (from Ref. 8).

suspended solids, bubbles and background light absorption.

5.1 Advantages and Limitations

Non-phenolic substances commonly encountered in water and wastewater generally do not interfere with this method, since few non-phenolics show such a change in UV absorption under the conditions employed. Consequently, the method is highly selective for individual phenols or mixtures of phenols having *similar* UV spectra.

It is important, however, to know which phenols are present in the sample so that the UV spectrum of each phenol can be checked for compatibility with the measuring wavelength. For example, *p*-methoxy phenol is unsuited for analysis at λ_{meas} = 289 nm because λ_{max} of the acid form = 288 nm, whereas λ_{max} of the base form = 305 nm. Thus absorption measured at λ_{meas} = 289 nm actually decreases as the pH is adjusted from 5 to 12. This reverse effect would defeat the analytical procedure by causing low readings for other phenols present.

If the instrument can be set at a longer measuring wavelength (e.g., λ_{meas} = 313 nm for mercury vapor lamps), *p*-methoxyphenol and other phenols having comparable λ_{max} values may be determined separately in a procedure similar to that of the common phenols. However, the analysis of unknown phenols with disparate λ_{max} values poses serious ambiguities with this method.

5.2 Instrumentation

Currently there are two different instruments specifically designed to analyze phenols by UV absorption according to pH (Ref. 8, 9). Each is described here and in the instrument notes. Ordinary UV spectrophotometers do not appear to be useful for this method.

5.2.1 Automatic Stream Monitor. The DuPont Model 450 Phenol Analyzer System is designed to monitor phenols directly and automatically in waste water streams (Ref. 8). The system uses UV light produced from a mercury vapor lamp. Measuring and reference wavelengths (λ_{meas}, λ_{ref}) are those shown in Figure B-5.

Figure B-6 is a schematic of the optical system and associated electronics. By using specific mercury wavelengths for λ_{meas} and λ_{ref}, along with special logarithmic amplifiers, phenols can be monitored with an accuracy of ±2% of full scale with sample background light transmission < 1% at λ_{meas} . As shown in Figure 6, UV light from the mercury vapor lamp passes through the water sample and is split into two beams. The first beam is reflected through an optical filter which transmits only λ_{meas} = 289 nm. The second beam is filtered of all but λ_{ref} = 365 nm. Each beam falls on a separate phototube detector. The two phototube signals are processed electronically by the logarithmic amplifiers and combined to provide a differential output which is linearly proportional to the phenol concentration. Phenols can be monitored over a sample span of approximately two orders of magnitude in phenol concentration. Several monitoring spans are available -- 2 to 100 μg/l is minimum, 0.2 to 10 mg/l is typical, others are available.

Figure B-7 shows the flow diagram of the automatic sampling system of the DuPont model 450. It operates on a ten minute cycle. After a brief sample flush through the system, 20% acetic acid (HAc) is mixed with the sample to adjust the pH to approximately 5. This sample is used to set the zero point on the recorder automatically. After zero-standardization, HAc flow to the sample stream ceases and is replaced by 20% sodium hydroxide (NaOH). The presence of base (pH 12) assures complete conversion of any free phenols to the corresponding phenolate anion. Any increase in UV absorption at the 289 measuring λ is interpreted as resulting from converting the phenols to phenolates (Figure B-8). Thus, the difference in absorption at 289 nm between the acidic and alkaline solutions is proportional to the phenol concentration(s). The scale of the recorder is calibrated with an optical filter corresponding to a definite phenol concentration. Such calibration can be checked readily with standard phenol solutions.

5.2.2 Laboratory Phenol Analyzer. The Spectro Products Model PH-1 phenol analyzer is designed for convenient and sensitive laboratory determination of phenols (Ref. 9). In some respects the PH-1 procedure is very similar to that of the previous instrument, viz.:

a. $\lambda_{meas} \approx 290$ nm, $\lambda_{ref} \approx 360$ nm;

b. zero adjustment of scale with the acidified (pH 4) sample;

c. net phenol determined from change in absorption at λ_{meas} after sample is made basic (pH 12).

However, with the model PH-1 all operations are manual rather than automatic. Also, the design of the instrument is different and prior distillation is advised for turbid samples.

Figure B-9 shows a block diagram of the PH-1. Note that a single phototube is employed for light detection. In order to accomplish ratio photometry of the light intensity at λ_{meas} and λ_{ref} , two light sources (lamps A and B) are alternately energized by a 400 Hz square wave power supply. The intensity of lamp A (source of λ_{meas}) is balanced against the intensity of lamp B (source of λ_{ref}).

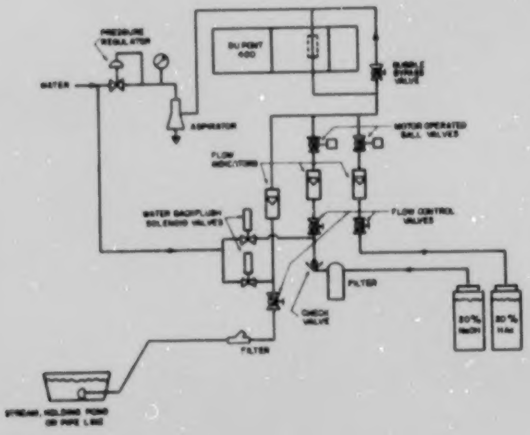


FIGURE B-7. *Sample flow diagram for DuPont Model 450 Phenol Analyzer System (from Ref. 8).*

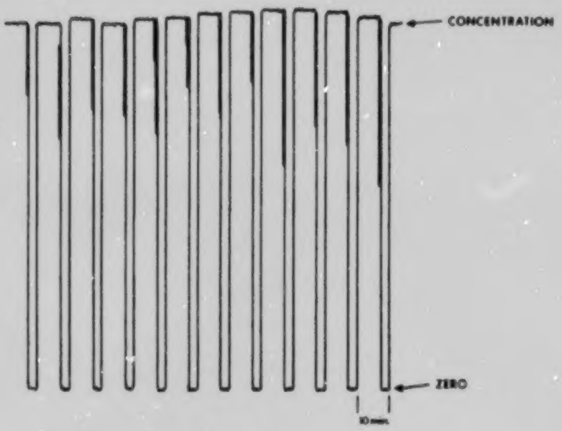


FIGURE B-8. *Typical Recorder Chart for DuPont Model 450 Phenol Analyzer (from Ref. 8).*

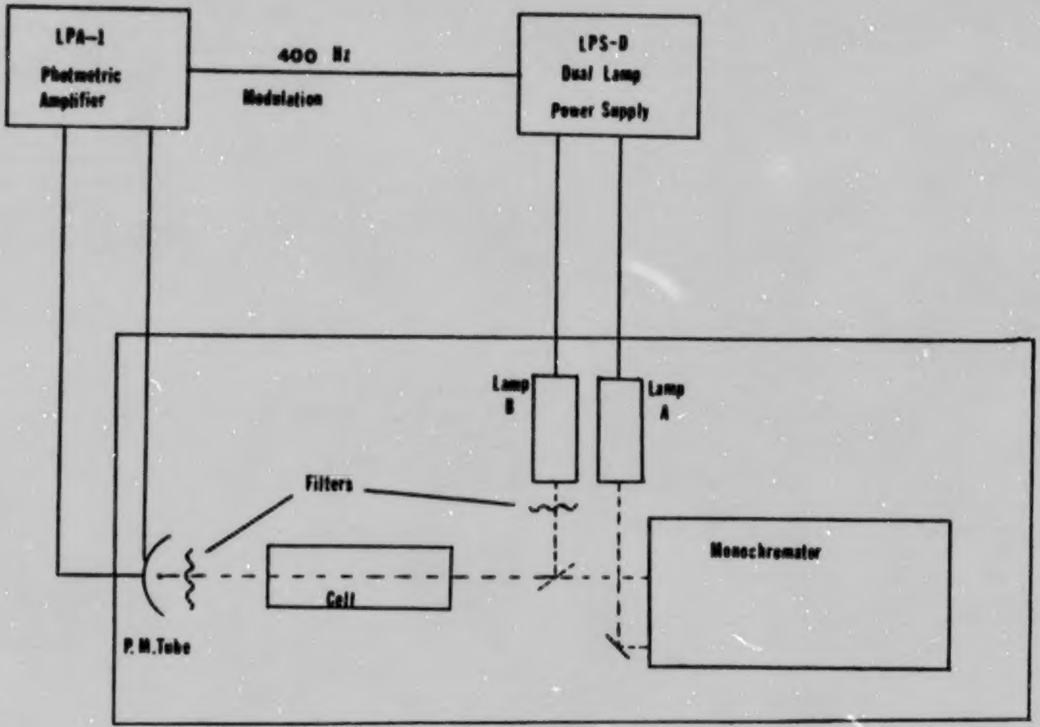


FIGURE B-9. Schematic diagram of Spectro Products Model PH-1 (from Ref. 9).

This is done by zeroing the read out meter with the acidified sample or standard placed in the beam path. When the beam from lamp A is blocked, no light is transmitted, so the meter is adjusted to read 100% absorption under these conditions.

Dependable, constant intensity hollow cathode lamps employed in atomic absorption spectroscopy provide the measuring and reference beams. To stabilize the lamp characteristics, a small dc voltage is also applied to them during the "off-cycle" to maintain partial emission. Lamp A uses three lines from the platinum spectrum (289.4, 289.8 and 293.0 nm) for the measuring beam and lamp B uses three lines from the chromium spectrum (357.9, 359.3 and 360.2 nm) for the reference beam. A monochromator and filters minimize unwanted light.

To avoid introducing unpredictable variables, all photometric measurements must be performed using the same sample cell in the same sampling position. One way to accomplish this is to take the "zero adjust" reading on the acidified sample (pH 4), then add 1 - 3 drops of 4 M NaOH (depending on cell size) to adjust pH $>$ 12. Since the instrument must be calibrated from standard phenol solutions, the same cell must be placed in the same position each time. Precise alignment and operator attention are required for best results.

The Spectro Products model PH-1 phenol analyzer has been evaluated by Keliher and co-workers (Ref. 9). Table B-7 shows the instrument performance for fifteen phenol calibrations each at four different concentrations.

A test mixture of likely phenol pollutants (60%) phenol, 15% *o*-cresol, 15% *m*-cresol and 10% *p*-cresol) was analyzed by both the standard 4-AAP method and the model PH-1 method (Ref. 6). The results of ten analyses by each method at six different concentrations are shown in Table B-8. The distillate from each sample was divided and analyzed by both methods. As anticipated, the results of the 4-AAP method

TABLE B-7.

Model PH-1 Precision According to Phenol Concentration for Fifteen Standard Samples (from Ref. 9)

	Phenol, μg/l			
	200	100	50	10
Mean % Absorption	10.44	5.55	2.92	0.66
Standard Deviation	0.216	0.192	0.190	0.13
Relative Standard Deviation	2.0%	3.4%	6.5%	19.7%

TABLE B-8.

Comparison of Standard 4-AAP Method and Model PH-1 Method for Phenols (from Ref. 9)

Concentration Added* To Blank Water μg/l	Standard 4-AAP Method			Ultraviolet Ratio Method		
	Mean of Ten	± Std. Dev.	% Rel. Std. Dev.	Mean of Ten	± Std. Dev.	% Rel. Std. Dev.
500	451.5	25.4	5.63	491.7	9.15	1.86
150	119.5	6.01	5.03	141.7	6.62	4.67
50	40.4	5.12	12.7	48.2	3.66	7.59
25	19.8	1.25	6.30	24.6	2.16	8.78
15	11.4	0.84	7.40	13.1	2.28	16.4
5	6.7	1.69	25.2	5.1	2.00	39.2

*Synthetic Mixture Consisting of: 60% Phenol
15% *o*-Cresol
15% *m*-Cresol
No Reaction with 4-AAP —— 10% *p*-Cresol

read consistently lower than either the model PH-1 or the actual value (except at the lowest concentration, 5 μg/l). No doubt this is partly due to the non-reactivity of one of the components, *p*-cresol, with the 4-AAP reagent. These data indicate that with a known test mixture of four phenols, fairly dependable determinations can be made with the Spectro Products model PH-1 instrument down to about 25 μg/l total concentration. Eleven unknown environmental samples were also analyzed (Table B-9).

TABLE B-9.

Analysis of Environmental Samples (from Ref. 9)

Sample	Location	Date Collected	4-AAP Method μg/l	PH-1 Method μg/l
1.	Stream - Ithan Road & Bridge Booth School	1/17/73	11	11
2.	Stream - Bryn Mawr	1/17/73	8	7
3.	Schuylkill River Conshochocken (running water)	2/6/73	16	20
4.	Schuylkill River Conshochocken (running water)	2/14/73	20	27
5.	Schuylkill River Conshochocken (still water)	2/14/73	22	32
6.	Philadelphia Public Water Supply, Overbrook Area (tap water sample)	4/6/73	14	22
7.	Villanova University (tap water sample)	4/6/73	18	28
8.	Schuylkill River Conshohocken (running water)	4/6/73	16	24
9.	Stream - Evens Road & Gypsy Hill Road, Gwyneed Valley, PA	4/6/73	10	15
10.	West Virginia Industrial Plant Influent	4/10/73	11.8×10^3	15×10^3
11.	West Virginia Industrial Plant Effluent (Influent after treatment)	4/10/73	5.5×10^3	8×10^3

6. Gas Chromatography of Pentafluorobenzyl Ether Derivatives

Kawahara (Ref. 10, 11) has described an analytical procedure for sensitive (ng/l) detection and identification of phenols in the presence of gross contamination. Several steps are involved:

a) separation of organic pollutants by organic solvent extraction (Ref. 11) or carbon adsorption (Ref. 10);

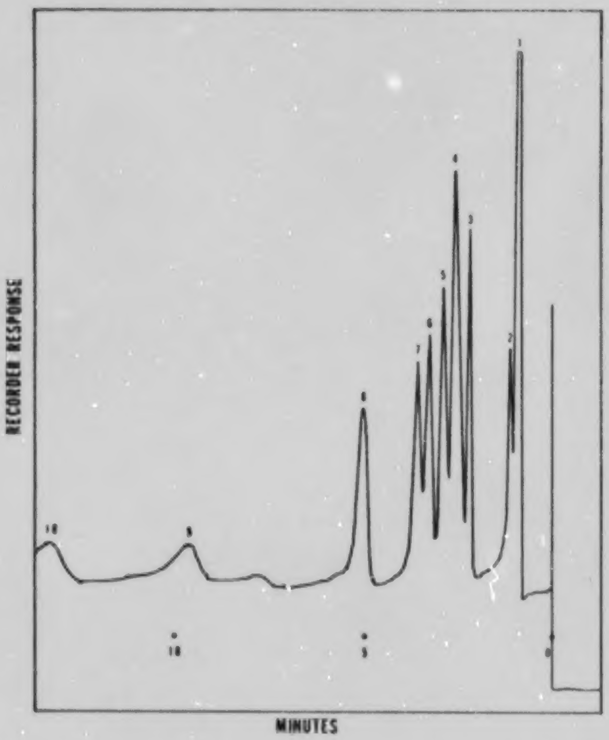
b) separation of the weak acids, mostly phenols and thiols, from other organics (strong acids, bases, neutrals);

c) derivatization of the weak acid fraction with pentafluorobenzyl bromide (α-bromo-2,3,4,5,6-pentafluorotoluene);

d) gas chromatography of the resulting pentafluorobenzyl aryl ether and thio ether derivatives using an electron capture detector (ECD).

With this procedure it is possible to detect and tentatively identify nanogram quantities of phenols from environmental samples. Figure B-10 is an ECD gas chromatogram of the pentafluorobenzyl ether derivatives of ten phenols starting with 0.32 ng of each. A shorter version (8 ft) of column No. 3 (section 3.3) was used.

As might be expected, the number of laboratory steps limits the utility of this method for general quantitative determinations. A few environmental samples have been analyzed. More extensive studies on environmental samples, with phenol standards added, would be desirable.



1. Solvent
2. Reagent
3. Phenol
4. *o*-, *m*-, *p*-Cresol
5. 2,4-Dimethyl Phenol
6. 2-Chlorophenol
7. 4-Chlorophenol
8. 2,4-Dichlorophenol
9. 2-Naphthol
10. 4-Chloro-2-Nitrophenol

FIGURE B-10. ECD gas chromatogram of pentafluorobenzyl ether derivatives of phenols using an 8-ft length of column No. 3 (from Ref. 11).

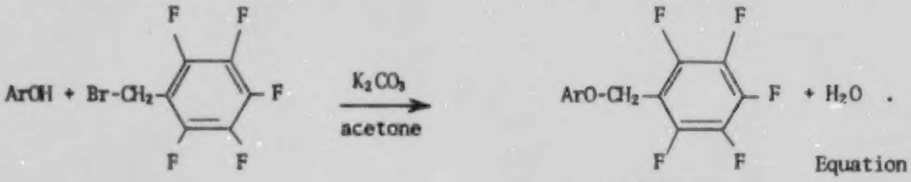
6.1 Phenol Isolation

Kawahara has employed both direct solvent extraction with 15% dichloromethane in hexane (Ref. 11) and the carbon adsorption procedure (Ref. 10) to separate phenols from water samples. These procedures are very similar to those discussed and referenced under Pesticides, Part B (H2O-PES, Methods, Section 3) to which the reader is referred.

Following extraction, the organic phase obtained by either procedure is chemically fractionated to separate the weakly acidic compounds (e.g., phenols, thiols) from other interfering organics (strong acids, neutrals and bases). Strong acids are easily extracted from the organic phase with bicarbonate solution. Most carboxylic acids and a few phenols (e.g., 2,4-dinitrophenol, 2,4,6-trinitrophenol) are completely removed in several extractions. Phenols (and thiols, if present) can then be extracted from the remaining neutral and basic organic compounds with dilute alkali (2 - 5% aq. NaOH). The free phenols and other weak acids are isolated from the alkaline extract by acidification (pH < 4) and extraction with organic solvent such as 15% dichloromethane in hexane. The organic residue after solvent evaporation contains only phenols and other weak acids. This organic fraction is derivatized with pentafluorobenzyl bromide for GC analysis.

6.2 Phenol Derivatization

Pentafluorobenzyl ether derivatives of phenols are formed in reaction with pentafluorobenzyl bromide (α-bromo-2,3,4,5,6-pentafluorotoluene) under alkaline, anhydrous conditions as shown in Equation 2:



Equation 2.

Kawahara reported generally good yields (84 to 99%) for the reaction with 0.8 mg each of phenol and 16 common substituted phenols. Only the extremely hindered di-t-butyl phenol gave a low yield (60%).

6.3 ECD-GC Analysis

Excellent analytical sensitivity (< 1 ng) is obtained by converting phenols to their pentafluorobenzyl derivatives. The pentafluorobenzyl group permits a 400- to 1000-fold greater sensitivity with the ECD than is obtainable with the FID for phenols (Ref. 11). This facilitates phenol detection and tentative identification in the presence of background impurities. The smaller GC sample requirement minimizes residue buildup in the gas chromatograph.

A gas chromatogram of the derivatives of typical phenols is shown in Figure B-10. Kawahara has also used a mixture of methylsilicone and fluorosilicone GC column packings to separate these and other derivatives (Ref. 10).

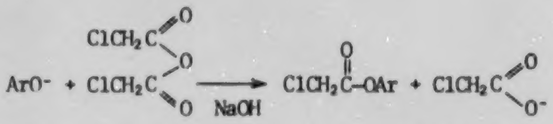
6.4 Advantages and Limitations

The high sensitivity of this ECD-GC method makes it attractive for ultra-trace detection and tentative identification of phenols in water. However, laboratory skill is required to perform the analytical steps properly. Also, pentafluorobenzyl bromide is a powerful lachrymator which requires exceptional care in handling. This reagent is also somewhat unstable on exposure to light and humidity.

The published chromatograms of environmental samples analyzed by this method do not appear to be as free from background interference as would be desired (Ref. 10, 11). Further refinement of the analytical procedure with typical environmental samples should be studied, particularly the GC conditions.

7. Gas Chromatography of Chloroacetate Ester Derivatives

Argauer (Ref. 12) has described a similar, but more direct, procedure for derivatizing phenols for analysis by ECD-GC. Phenols are not extracted from the water samples (15 to 150 ml) but are treated directly with 10 ml of a 0.5% solution of chloroacetic anhydride in benzene in the presence of 150 mg of sodium hydroxide. The sodium hydroxide (alkali) maintains the phenols in their phenolate anion form which reacts readily with the chloroacetic anhydride according to Equation 3:



$$\mathrm{ArO^- + (ClCH_2CO)_2O \xrightarrow[NaOH]{} ClCH_2C(=O){-}OAr + ClCH_2CO_2^-}$$

Equation 3.

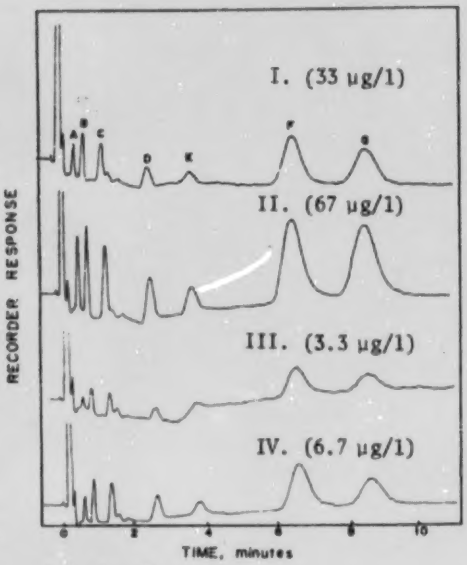
Since the esterifying reagent (chloroacetic anhydride) and its solvent (benzene) are not very soluble in water the reaction requires vigorous shaking. The derivatization is relatively rapid but if shaking of the reaction mixture continues beyond two minutes, losses of chloroacetate esters occur, notably those of phenol, *p*-cresol and *p*-chlorophenol. Presumably this is the result of saponification (hydrolysis) catalyzed by the alkali present. Better reaction conditions are required for this method to be quantitative for these phenols.

The phenol chloroacetate derivatives are analyzed by ECD-GC by direct injection of a 5-μl aliquot of the benzene phase from the reaction mixture. Figure B-11 shows ECD gas chromatograms of the chloroacetates derived from seven phenolics. Argauer (Ref. 12) includes GC retention data for thirty-four phenolic chloroacetate derivatives chromatographed on a cyanosilicone column. Values for ten of these derivatives are non-unique, i.e., ambiguous.

Detection sensitivity approaches the ng/l level for these phenolic standards. No studies were performed on raw water or waste water samples, but if previous experience is any guide, complications may be anticipated for such samples.

8. UV Fluorescence Spectroscopy

Preliminary studies on the use of UV fluorescence of phenols indicates that this technique could be utilized for the measurement of phenols in water (Ref. 13). Upon UV irradiation, phenols absorb some of the UV energy through excitation processes. A portion of the absorbed energy is re-emitted spontaneously by excited phenol molecules. This UV emission process is called fluorescence. Emission from an irradiated phenol sample is



A = phenol
B = *p*-cresol
C = 3,4-xylenol
D = 4-(di-methylamino)-3,5-xylenol
E = eugenol
F = 1-naphthol
G = pentachlorophenol

FIGURE B-11. Gas chromatograms of chloroacetate derivatives separated on a 5-ft cyanosilicone column (from Ref. 12).

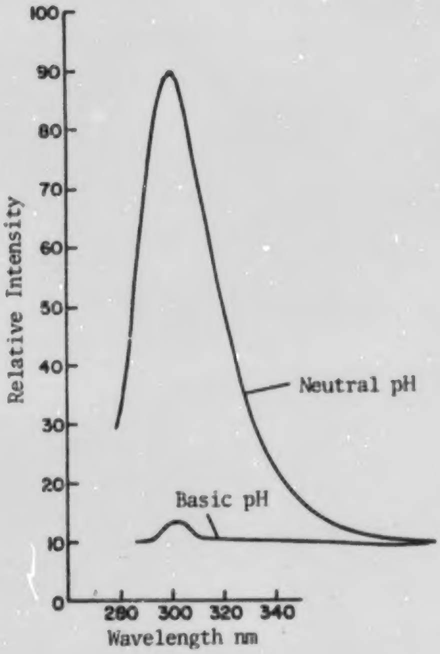


FIGURE B-12. Fluorescence emission of p-cresol 1 mg/l in water λ_{ex} 275 nm (from Ref. 13).

detected at right angles to the incident UV radiation.

There are two types of fluorescence spectroscopy: (a) emission and (b) excitation spectroscopy. The technique described here utilizes emission spectroscopy, i.e., the phenol sample is excited at a specific selected wavelength while the wavelength of the UV emission is scanned. The emission spectrum is simply the record of emission intensity plotted as a function of the detection wavelength (λ). The excitation wavelength (λ_{ex}) is generally chosen to approximate the λ_{max} of the UV absorption spectrum of the substance. As discussed in section 4, phenols have two different λ_{max} in aqueous solution, depending on the pH (see Fig. B-5). Only the λ_{max} for the free phenol (acid form) is relevant for the fluorescence method, since the phenolate anion (base form) does not exhibit UV fluorescence (see Fig. B-12). This characteristic can be used to distinguish between fluorescence due to phenolics and background fluorescence by simply making the sample alkaline ($pH \geq 12$) after taking the spectrum under neutral or acidic conditions (pH 4 to 7). The alkaline spectrum is subtracted from the normal spectrum to derive the net fluorescence due to phenol.

In cases where only a single, known phenol is present, this method would appear to be reasonably fast, simple and accurate down to μg/l phenolic concentrations. Frequently, however, several phenols need to be monitored simultaneously in waste water. If these phenols have very similar UV emission intensities at a given λ_{ex}, they could be determined as an aggregate. In this regard, Kullbom et al. (Ref. 13) have examined the emission spectra of phenol and the cresols in water at mg/l concentrations. Spectra of these four phenolics at λ_{ex} = 270, 275 nm (Figure B-13, a and b, respectively) are sufficiently similar to determine them as an aggregate, although many environmental examples should be studied. This is especially true for waste water samples because of the notorious tendency of UV fluorescence to be quenched by extraneous contaminants.

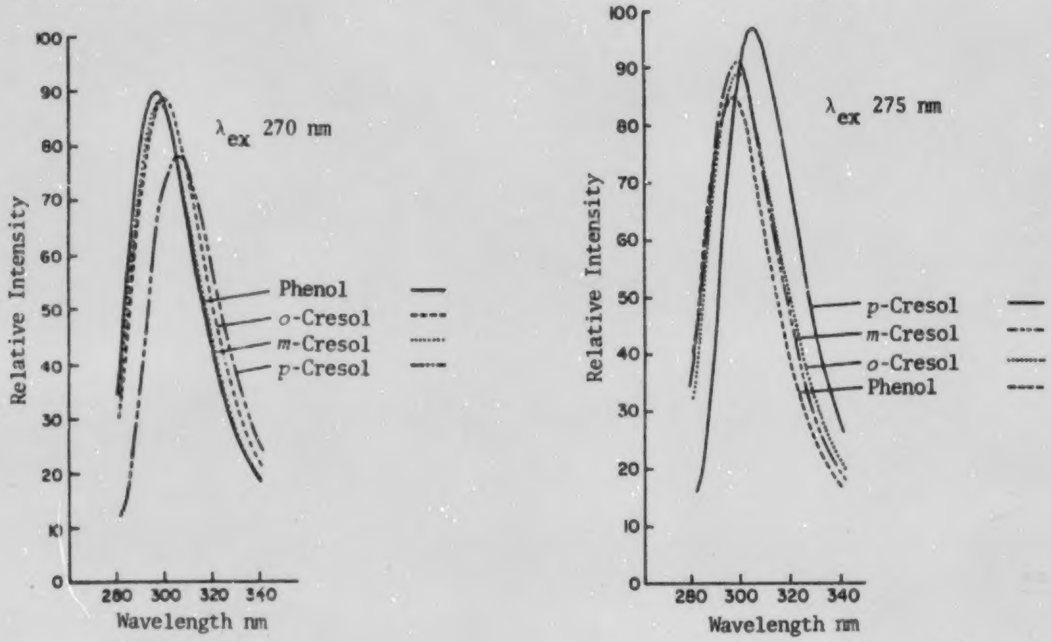


FIGURE B-13(a).

FIGURE B-13(b).

FIGURE B-13. Fluorescence emission of phenol and cresols, 1 mg/l in water (from Ref. 13).

9. Gas Chromatography-Mass Spectrometry (GC-MS)

Gas chromatographic separation of sample components coupled with direct mass spectrometric identification is a powerful analytical tool for organic compounds in general. Aspects of GC-MS are discussed under part B of Pesticides (H2O-PES, Methods, Section 9). Principles described there for pesticide analysis apply equally to phenols. For example, a phenolic compound may be readily identified directly from its mass spectrum if the gas chromatogram is relatively well defined. Where sample mixtures are too complex for satisfactory GC separation or if GC background interferences are serious, the GC-MS system, aided by computer data handling, can still detect and identify phenols (or suitable derivatives) by searching for mass spectral peaks characteristic of the various phenols.

GC-MS-Data systems rank among the most expensive analytical instruments (ca. $100,000), so the number of such facilities available for phenol analysis would be expected to remain limited. It is pertinent to note, however, that GC-MS instrumentation is now common in the EPA laboratories. GC-MS is perhaps best utilized for analysis of suspected phenolics associated with (a) unusual pollution incidents, (b) previously uninvestigated pollution situations, or (c) extremely difficult samples. Once the offending phenolics have been identified satisfactorily, monitoring them on a routine basis may be transferred to less expensive instrumental techniques.

10. Summary and Conclusions

The four spectrophotometric methods (4-AAP, MBTH, UV absorption, UV fluorescence) are relatively simple and fast. They are best employed in routine sampling where the phenolic components and interfering substances are generally well known from other, more detailed analyses. All four have certain limitations which must be taken into consideration:

a) 4-AAP Method. Many *para* substituted phenols fail to form the characteristic dye and hence escape measurement.

b) MBTH Method. Most *para* substituted phenols give a reduced response, some fail to form the characteristic dye.

c) UV Absorption. Phenols having a λ_{max} for the free acid form very near the measuring λ (e.g., *p*-methoxy-phenol) can cause low readings for most common phenols.

d) UV Fluorescence. It is well known that impurities can seriously affect the UV fluorescence of organic compounds. Further study of this technique with actual waste water conditions is needed to determine what interferences will cause problems.

The 4-AAP and the MBTH methods have comparable sensitivity for most phenolics which are detected by both methods. The lower limit of detection is about 0.2 µg/l when samples are distilled before the dye reaction and extracted into chloroform afterwards (Ref. 7).

The gas chromatographic methods provide qualitative information on the number and identity of phenols present in addition to providing a quantitative determination. The direct method is very convenient for analyzing water samples which are free of organic compounds with GC retention times similar to those of the anticipated phenols. Sensitivity in the absence of such serious interference is about 1 mg/l without sample cleanup or enrichment. If phenol concentrations are lower, or if organic interferences are serious, the phenolics should be extracted from the water sample and chemically separated into a weak acid fraction before GC analysis.

Where qualitative identification is more important than quantitative determination, the phenolics may be better analyzed by derivatization as the pentafluorobenzyl ethers for highly sensitive ($<$ ng/l) detection by ECD-GC. However, this procedure is probably too elaborate for routine waste samples. For this purpose a faster, simpler but less accurate alternative is the chloroacetate procedure. It involves direct derivatization of the aqueous phenols to their chloroacetate esters followed by direct injection of the organic phase into ECD-GC. The instability of some phenol esters to the reaction conditions limits this method to qualitative and semi-quantitative applications.

The ECD-GC procedures and GC-MS are best applied to newly investigated situations where high sensitivity and qualitative identification are needed. The ECD-GC methods require less instrumentation than GC-MS but are less rigorous. ECD-GC can be performed on equipment used for routine pesticide analyses. The GC-MS method assisted by computer data handling techniques represents the ultimate in presently available analytical instrumentation. It should be reserved for situations which require ultrasensitive, highly rigorous identifications and measurements on extremely difficult samples. GC-MS analysis can be performed at EPA Regional Technical Support Laboratories under appropriate circumstances.

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8. Bulletins 400-A and 450, E.I. DuPont de Nemours and Co. (Inc.), Instrument Products Division, Wilmington, DE 19898, or Monrovia, CA 91016.

9. J.E. Fountaine, P.B. Joshipura, P.N. Keliher and J.D. Johnson, "New Ultraviolet Ratio Spectrophotometric System for the Determination of Trace Amounts of Phenolic Compounds," Anal. Chem. 46 , 62 (1974).

10. F.K. Kawahara, "Microdetermination of Phenols and Mercaptans by Means of Electron Capture Gas Chromatography," Anal. Chem. 40, 1009 (1968).

11. F.K. Kawahara, "Gas Chromatographic Analysis of Mercaptans, Phenols and Organic Acids in Surface Waters with Use of Pentafluorobenzyl Derivatives," Environ. Sci. and Technol. 5, 235 (1971).

12. R.J. Argauer, "Rapid Procedure for the Chloroacetylation of Microgram Quantities of Phenols and Detection by Electron Capture-Gas Chromatography," Anal. Chem. 40, 122 (1968).

13. S.D. Kullbom, H.F. Smith and P.S. Flandreau, "Fluorescence Spectroscopy in the Study and Control of Water Pollution," Paper no. 288 presented at the 1970 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, by the Perkin-Elmer Corporation, Norwalk, CT 06852.

14. Handbook for Analytical Quality Control in Water and Wastewater Laboratories, Environmental Protection Agency, U.S. Government Printing Office, Washington, DC 20402 (1972).

15. "The Role of Automated Wet-Chemical Analysis in Environmental Studies," Technicon Corporation, Tarrytown, NY 10591 (1969).

16. "Phenol in Water and Waste Water," Industrial Method AAII, 127-71W, Technicon Corporation, Tarrytown, NY 10591 (Sept. 1971).

17. Private communication from Morris Gale, Methods Development and Quality Assurance Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, OH 45268 (April, 1974).

18. Private communication from E.W. McFarren, Methods Development and Quality Assurance Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, OH 45268 (April, 1974).

19. R.A. Baker, "Phenolic Analyses by Direct Aqueous Injection Gas Chromatography," J. Amer. Water and Wastewater Assoc. 58, 751 (1966).

12. PHENOL INSTRUMENT NOTES

The direct laboratory analysis of phenols by gas chromatography (sec. B. 3) employs conventional gas chromatographs equipped with flame ionization detectors (GC-FID). Four isothermal gas chromatographs are listed in this section. Additional temperature programmable gas chromatographs are listed among the instrument notes under oil and grease (H20-OIL, sec. B. 8). [Note: temperature programming is not required for phenols but it is extremely useful for many other GC applications.]

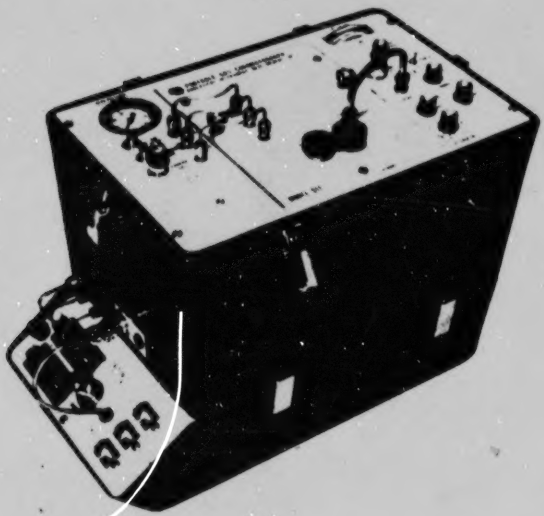
Where extreme sensitivity is desired, analysis of halogenated derivatives of phenols by electron capture gas chromatography (GC-ECD) has been suggested (sec. B.6-7). For examples of suitable gas chromatographs the reader is referred to the Pesticides instrument notes (H20-PES, sec. B. 12) under the category: Principle of Operation: GC-ECD.

Combined gas chromatograph/mass spectrometers will also be listed with the Pesticide instruments. Although GC/MS is not required for current standard phenol analyses, GC/MS is an important general technique for many organics, phenols included.

The remaining instruments listed in this section are the colorimetric analyzers used in the official EPA 4-AAP method (sec. B. 2 and Appendix I) and the ultraviolet spectrophotometers which measure the shift in UV absorbance with a change in pH (sec. B.5).

The Instrument notes are arranged alphabetically by manufacturer and each model has been assigned a number. The manufacturer's specifications have been published as available, and we gratefully acknowledge that all manufacturers have assisted in the compilation of their notes. All information has been supplied by the manufacturer, either from brochures and instruction manuals or by private communication with the manufacturer. If no information is given for a particular instrument specification, this indicates that none was available.

Phenol Analyzer
Gas Chromatograph Model 511



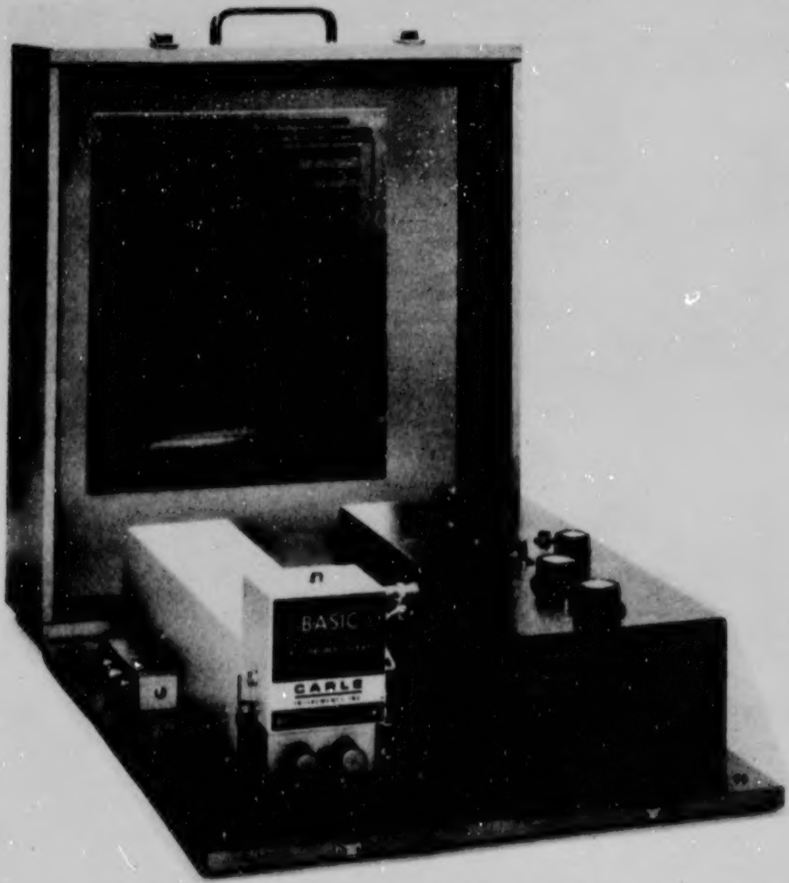
Class	Field or Laboratory: Routine analysis
Principle of Operation	Gas Chromatography - Flame Ionization Detection (GC-FID)
Sensitivity	1 x 10^{-11} g/sec hydrocarbon (0.02 coulombs/g carbon) minimum
Range	10^{-6} to 10^{-11} hydrocarbon
Interferences	Appreciable interferences from organic compounds in general Moderate interferences from GC column and septum bleed Slight or no interferences from H_2O, CO_2, CO, COS, CS_2, SO_2, N_2, Ar, He, Ne, among others
Multi-Parameter Capability	Can be operated as a total hydrocarbon, methane or nonmethane hydrocarbon analyzer; convertible to ECD, FPD and TCD.
Sampling	Method: Syringe injected aliquot of water sample or solvent extract
Sample Inlet	Type: Silicone rubber septa, screw-cap retained on Teflon injection ports, 1/8" size On-column injection: Standard, 1/8" Glass Liners (inserts): Not available Capillary columns: Not available Temperature range: Within 5° of column oven temperature Temperature regulation: controlled from column oven circuitry Overheat protection: Fail safe circuitry

Column Oven	Type: Single column, injection port and detector; packed metal, glass or Teflon column, vertically coiled; convection conduction heated Carrier gas: He or N_2, prepurified Flow control: Differential flow regulator Flow range, tolerance: 0.3% Flow calibration: Optional soap bubble flowmeter required Column capacity: Standard, 1/8" O.D. metal tubing, 1 ea.: 6' Optional, 1/8" O.D. metal tubing, 2 ea.: 30'with column switch valve. Temperature range: Continuously adjustable, ambient to 200°C Temperature regulation: DC proportional controller, ±0.1°C constant ambient Overheat protection: Fail safe circuitry Optional temperature program: None
Detector	Type: Single flame ionization (FID) Temperature range: Within 5°C of column oven temperature Temperature regulation: Controlled from column oven circuitry Overheat protection: Fail safe circuitry Accessory gas flow: ca. 25 cc/min prepurified H_2; ca. 120 cc/min prepurified air Linear dynamic range: 10^5
Detector Amplifier	Type: FET, single channel Sensitivity: 5×10^{-12} A full scale Linear dynamic range: Greater than 10^6 Drift: 5×10^{-14}A per hour @ constant ambient Noise: 10^{-13} A peak to peak Background suppression: 0 to $\pm 10^{-6}$ A with coarse and fine adjustment Attenuation: Input (range), X1, X100, X10,000 Output (attenuator), X1, X2, X4,.....X1024 Outputs: For recorder, 1 mV Time constant: 0.5 sec
Requirements	Pressure regulated gas supplies: 0 to 60 psig He or N_2; 0 to 60 psig H_2; 0 to 60 psig air; all gases, prepurified grade Power: 117 V, 50-60 Hz Size: 38.1 cm H, 45.7 cm W, 25.4 cm D (15" x 18" x 10") Weight: 17.1 kg (38 lb)
References	Manufacturer's product bulletin No. 131 and price list
Features	Portable, completely equipped, with gas bottles and rechargeable Ni-Cd batteries; optional back-flush and column switching valves
Cost	Gas chromatograph Model 511 $3,975.
Remarks	This portable model is also available for (a) laboratory bench use (Model 521) at $3,350 and (b) rack mount (Model 531) at $3,350.
Address	Analytical Instrument Development Inc. Rte. 41 & Newark Rd. Avondale, PA 19311 (215) 268-3181

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

H2O-PHE
Phenol Analysis
Carle 1
August 1975

Phenol Analyzer
Gas Chromatograph Model 9500

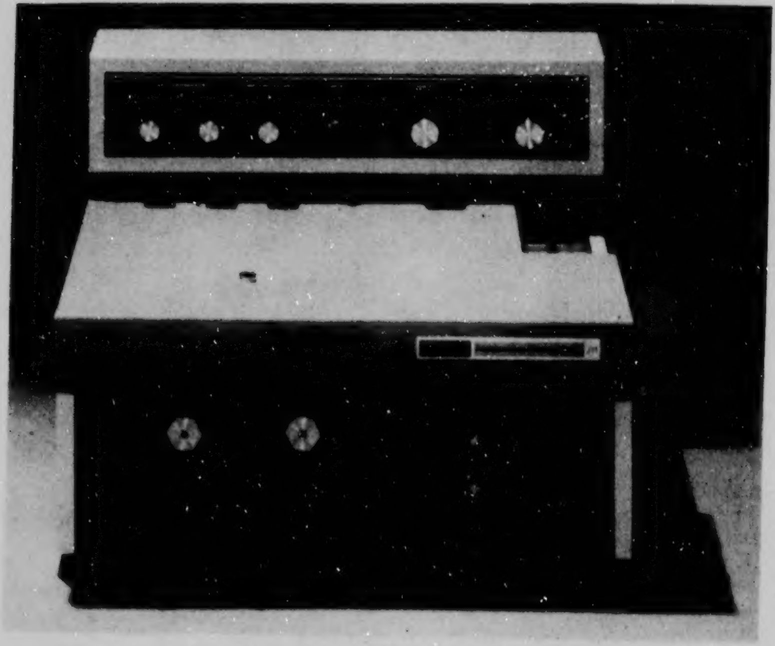


Class	Laboratory or Field: Routine analysis (field use requires external 117 V AC power)
Principle of Operation	Gas Chromatography - Flame Ionization Detection (GC-FID)
Sensitivity	1×10^{-11} g/sec hydrocarbon (0.016 coulombs/g carbon) minimum
Range	10^{-5} to 10^{-11} hydrocarbon
Interferences	Appreciable interferences from organic compounds in general Moderate interferences from GC column and septum bleed Slight or no interferences from H_2O, CO_2, CO, COS, CS_2, SO_2, N_2, Ar, He, Ne, among others
Multi-Parameter Capability	Can be operated as a total hydrocarbon analyzer
Sampling	Method: Syringe injected aliquot of water sample or solvent extract
Sample Inlet	Type: Silicone rubber septa, spring-loaded screw-cap retained on stainless-steel injection ports, 1/8" size On-column injection: Standard, 1/8" Glass Liners (inserts): Not available Capillary columns: Not available Temperature range: ca. 10°C higher than column oven temperature Temperature regulation: Line voltage dependent, ambient dependent Overheat protection: Line fuse only

Column Oven	Type: Dual columns and injection ports; single detector; packed metal or glass columns, vertically coiled; conduction/convection heated Carrier gas: He or N_2, prepurified Flow control: Optional regulators available Flow range, tolerance: temperature dependent Flow calibration: optional soap bubble flowmeter required Column capacity: Standard, 1/8" O.D. metal tubing, 2 ea.: 6' Optional, 1/8" O.D. metal tubing, 2 ea.: 24' maximum Temperature range: Continuously adjustable, ambient to 200°C Temperature regulation: Line voltage dependent, ambient dependent Overheat protection: Line fuse only Optional Temperature program: None
Detector	Type: Dual feed, single flame ionization (FID) Temperature range: Approximately 10°C higher than column oven temperature Temperature regulation: Line voltage dependent, ambient dependent Overheat protection: Line fuse only Accessory gas flow: ca. 20 cc/min prepurified H_2; ca. 365 cc/min prepurified air Linear dynamic range: 10^5
Detector Amplifier	Type: MOSFET, single channel Sensitivity: 5×10^{-12} A full scale Linear dynamic range: 10^5 Drift: less than 5×10^{-14} A/hr @ constant ambient Noise: 2×10^{-14} A Background suppression: 0 to $\pm 10^{-9}$ A with coarse and fine adjustment Attenuation: Input (range), X1, X100, X10,000, X1,000,000 Output (attenuator), X1, X2, X5, X10, X20, X50, X100, X200 Outputs: For recorder, 1 mV; 10 mV optional Time Constant: 0.5 sec max (Range 1); 0.1 sec nominal
Requirements	Pressure regulated gas supplies: 0 to 60 psig He; 0 to 60 psig H_2; 0 to 60 psig air; all gases, prepurified grade Power: 117 V, 50-60 Hz Size: 16 cm H, 41 cm W, 47 cm D (6-¼" x 16" x 18-½") Weight: 14.5 kg (32 lb)
References	Manufacturer's bulletin No. 9500
Features	Briefcase size, light weight for convenient carrying
Cost	Gas chromatograph Model 9500 $1185.00
Remarks	Regulating transformer assembly no. 8025 ($78.00) recommended for best temperature and baseline stability.
Address	Carle Instruments, Inc. 1141 E. Ash Ave. Fullerton, CA 92631 (714) 879-9900

H2O-PHE
Phenol Analysis
Carle 2
August 1975

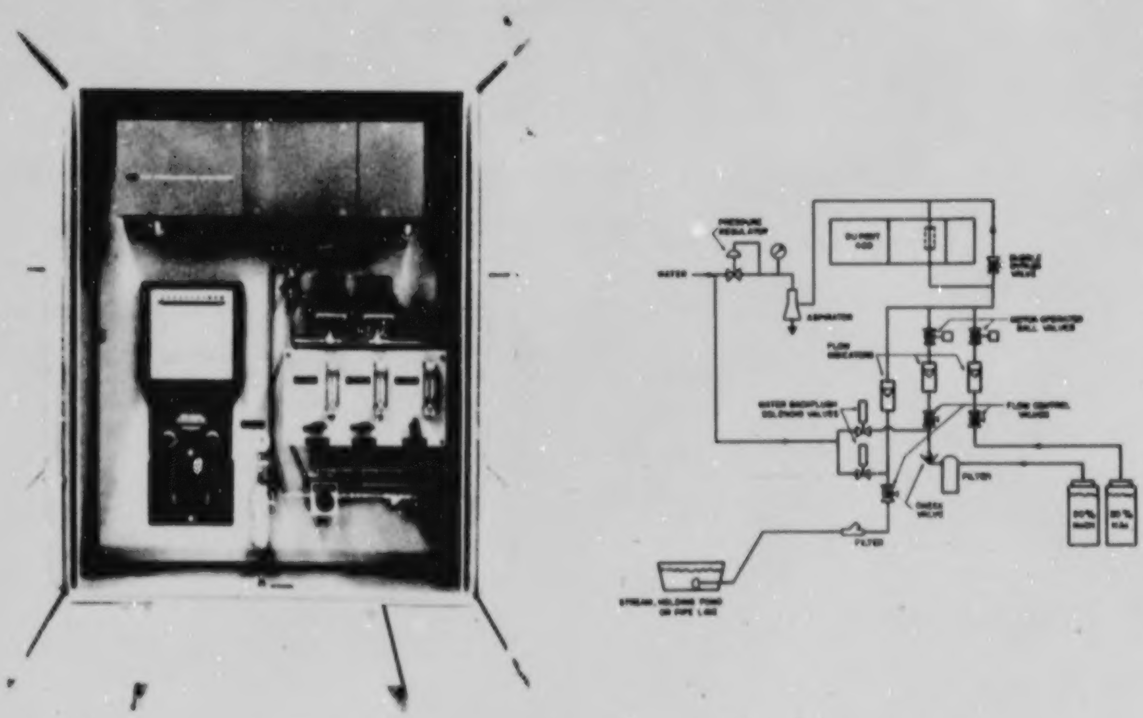
Phenol Analyzer
Gas Chromatograph Model AGC-211



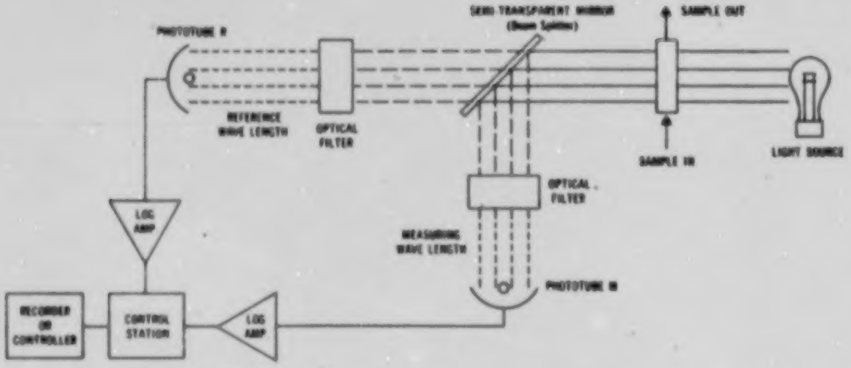
Class	Laboratory: Routine analysis
Principle of Operation	Gas Chromatography - Flame Ionization Detection (GC-FID)
Sensitivity	2.5×10^{-12} g/sec hydrocarbon (0.016 coulombs/g carbon) minimum
Range	10^{-6} to 10^{-12} g/sec hydrocarbon
Interferences	Appreciable interferences from organic compounds in general Moderate interferences from GC column and septum bleed Slight or no interferences from H_2O, CO_2, CO, COS, CS_2, SO_2, N_2, Ar, He, Ne, among others
Multi-Parameter Capability	None
Sampling	Method: Syringe injected aliquot of water sample or solvent extract
Sample Inlet	Type: Silicone rubber septa, spring-loaded screw-cap retained on stainless-steel injection ports, 1/8" size, standard; 1/4", 3/16", 1/16" optional On-column injection: Standard 1/8" Glass Liners (inserts): Not available Capillary columns: Not available Temperature range: ca. 35°C or 65°C higher than column oven temperature Temperature regulation: Controlled from column oven circuitry Overheat protection: Line fuse, plus thermal alloy burnout link

Column Oven	Type: Dual columns and injection ports; single detector; packed metal or glass columns, horizontally coiled; conduction/convection heated Carrier Gas: He or N_2, prepurified Flow control: Optional regulators available Flow range, tolerance: temperature dependent Flow calibration: optional soap bubble flowmeter required Column capacity: Standard, 1/8" O.D. metal tubing, 2 ea.: 24" Temperature range: Continuously adjustable in 1° increments from ambient to 399°C Temperature regulation: Fully proportional, ±0.01°C at oven floor Overheat protection: Line fuse, plus thermal alloy burnout link Optional Temperature program: None
Detector	Type: Dual feed, single flame ionization (FID) Temperature range: ca. 0° to 40°C higher than column oven temperature Temperature regulation: Controlled from column oven circuitry Overheat protection: Line fuse, plus thermal alloy burnout link Accessory gas flow: ca. 20 cc/min prepurified H_2; ca. 365 cc/min prepurified air Linear dynamic range: Greater than 10^6
Detector Amplifier	Type: Varactor bridge, single channel Sensitivity: 1×10^{-12} A full scale Linear dynamic range: Greater than 10^6 Drift: Less than 3×10^{-14} A/hr @ constant ambient Noise: 1×10^{-14} A Background suppression: 0 to $\pm 10^{-9}$ A with coarse and fine adjustment Attenuation: Input (range), X1, X10, X100, X1000, X10,000 Output (attenuator), X1, X2, X4......, X1024 Outputs: For recorder, 1 mV; 10 mV optional Time Constant: 0.5 sec max (Range 1); 0.1 sec nominal
Requirements	Pressure regulated gas supplies: 0 to 60 psig He; 0 to 60 psig H_2; 0 to 60 psig air; all gases, prepurified grade Power: 117 V, 50-60 Hz Size: 33 cm H, 44.5 cm W, 44.5 cm D (13" x 17.5" x 17.5") Weight: 21.6 kg (48 lb)
References	Manufacturer's bulletin No. 0101
Features	
Cost	Gas Chromatograph Model AGC-211 $2225.
Remarks	Model AGC-311 ($2975) has both FID and TCD
Address	Carle Instruments, Inc. 1141 E. Ash Ave. Fullerton, CA 92631 (714) 879-9900

Phenol Continuous Analyzer
Du Pont 450 Phenol Analyzer


PRESSURE REGULATOR
WATER
ASPIRATOR
DU PONT 400
AIR OPERATED BALL VALVES
FLOW INDICATORS
WATER BACKFLUSH SOLENOID VALVES
FLOW CONTROL VALVES
FILTER
CHECK VALVE
FILTER
STREAM, HOLDING POND OR PIPE LINE

Du Port 450 Phenol Analyzer System


PHOTOTUBE R
SEMI-TRANSPARENT MIRROR
(Beam Splitter)
SAMPLE OUT
REFERENCE WAVE LENGTH
OPTICAL FILTER
SAMPLE IN
LIGHT SOURCE
OPTICAL FILTER
LOG AMP
MEASURING WAVE LENGTH
PHOTOTUBE M
RECORDER OR CONTROLLER
CONTROL STATION
LOG AMP

Du Pont UV-400 Detector

Class	Continuous-Sensor, Stationary
Categories of Water	Fresh, Waste

Principle of Operation	UV absorption utilizing the characteristic wavelength shift of phenols according to pH. The sample stream is drawn through the system at pH 5 to zero the spectrophotometer at 289 nm with respect to the reference wavelength (365 nm). Then the system monitors phenol differential absorption at pH 12. The cycle is repeated every ten minutes.
Minimum Detectable Sensitivity	0.5 μg/ℓ
Range	0.5 - 50 μg/ℓ up to 0.01 - 1.0 g/ℓ phenol
Interferences	Compounds (including phenols) absorbing more at pH 5 than at pH 12 at measuring λ; dissolved SO_2, Cr^{+VI}, Fe^{III}.
Multiparameter Capability	None
Sampling	Method: Periodic (analysis approximately every 10 minutes), automatic Volume: 100-200 ml/min from bypass line Maximum Temperature Input: Ambient, 4°C - 50°C approximately Collection Efficiency: 100% Maximum Number of Sample Sources: 6 @ 3 min cycle
Performance	Accuracy: ±2% of full scale Reproducibility: 1% of full scale Linearity: 2% Noise: ±1% of full scale Lag Time: ∿ 1 min maximum Rise Time: 1 sec Fall Time: 1 sec Zero Drift: Automatic zeroing every cycle Span Drift: Less than 1%
Operation	Ambient Temperature Range: 4 - 50°C approx. Temperature Compensation: Automatic zero compensates for temperature changes Relative Humidity Range: 0 - 80% Calibration: Optical filter corresponding to a given concentration of phenol Procedure: Automatic Unattended Period: Daily check; ∿ 7 days between reagent changes Maintenance: Approximately 1 hr/week, mostly for routine checks and adjustments
Requirements	Power: 115 V ac, 60 Hz (50 Hz available); 500 W maximum Weight: Approximately 275 Kg (600 lb) Dimensions: 184 cm H × 122 cm W × 26 cm D (72" × 48" × 10")
Features	Output: 0 - 10 mV, others available Training: Available at standard rates Options: Other outputs, shorter sample cells
References	Manufacturer's brochure 450-A, reprint A-81345 R. S. Saltzmann et al., "Simplifying Sampling Problems with a Versatile Photometric Analyzer", DuPont Co. reprint A-72961
Cost	450 Photometric Analyzer $12,000 (approx) for single point
Remarks	For installation on waste bypass lines or holding ponds; reorder required
Address	E. I. du Pont de Nemours and Co. (Inc.) Instrument Products Division Wilmington, Delaware 19898 Attn: Robert S. Saltzmann (302) 772-5114 or Monrovia, CA 91016 (213) 357-2111

H2O-PHE
Phenol Analysis
Gow-Mac 1
August 1975

Phenol Analyzer
Gas Chromatograph Model 69-750

GAS CHROMATOGRAPH
GOW MAC

Class	Laboratory: Routine analysis
Principle of Operation	Gas Chromatography - Flame Ionization Detection (GC-FID)
Sensitivity	1 x 10^{-12} g/sec hydrocarbon (0.015 coulombs/g carbon) minimum
Range	10^{-6} to 10^{-12} g/sec hydrocarbon
Interferences	Appreciable interferences from organic compounds in general Moderate interferences from GC column and septum bleed Slight or no interferences from H_2O, CO_2, CO, COS, CS_2, SO_2, N_2, Ar, He, Ne, among others
Multi-Parameter Capability	None
Sampling	Method: Syringe injected aliquot of water sample or solvent extract

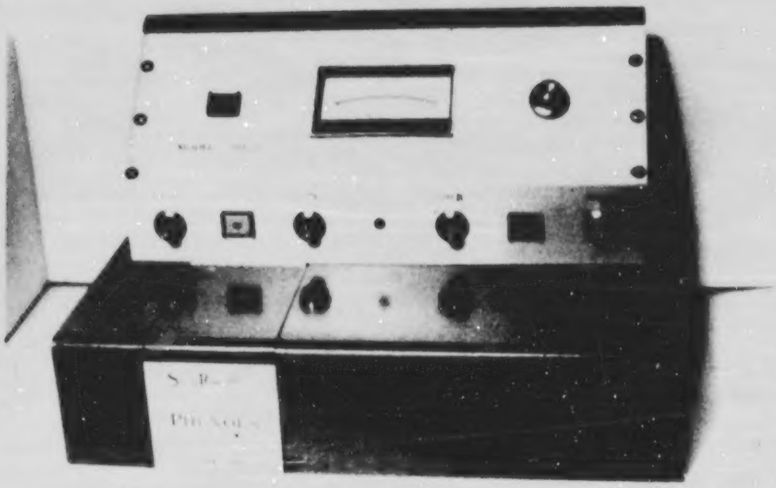
Sample Inlet	Type: Silicone rubber septum, screw-cap retained on a stainless-steel injection port, 1/8" size On-column injection: Standard Glass Liners (inserts): Yes Capillary columns: Not available Temperature range: Ambient to 300°C Temperature regulation: Variac, line voltage dependent Overheat protection: Line circuit breaker, 7A
Column Oven	Type: Single column, injection port and detector; metal or glass columns, horizontally coiled; forced air circulation Carrier gas: He or N_2, prepurified Flow control: Needle valve, or Flow Controller available Flow range, tolerance: temperature dependent Flow calibration: rotameters optional Column capacity: Standard, 1/8" O.D. metal tubing, 1 ea.: 50' Optional, 1/4" O.D. glass tubing, 1 ea.: 25' Temperature range: Continuously adjustable, ambient to 300°C Temperature regulation: Fully proportional, ±0.1°C Overheat protection: Line circuit breaker, 7A Optional temperature program: None
Detector	Type: Single flame ionization (FID) Temperature range: Ambient to 300°C Temperature regulation: Line voltage dependent Overheat protection: Line circuit breaker, 7A Accessory gas flow: ca. 30 cc/min prepurified H_2; ca. 500 cc/min prepurified air Linear dynamic range: 10^6
Detector Amplifier	Type: JFET Sensitivity: 1.5×10^{-12} A full scale Linear dynamic range: 1×10^6 Drift: 6×10^{-14} A/hr @ constant ambient Noise: 2×10^{-14} A Background suppression: 0 to $\pm 10^{-5}$ Attenuation: Input (range), ×1.5, ×15, ×150, ×1500 Output (attenuator), ×1, ×2, ×4,...×512 Output : For recorder, 1 mV; Time Constant: 0.5 sec nominal
Requirements	Pressure regulated gas supplies: 0 to 60 psig He; 0 to 60 psig H_2; 0 to 60 psig air; all gases, prepurified grade Power: 117 V, 50/60 Hz (230 V, 50/60 Hz optional); 900 W maximum Size: 43.2 cm H, 30.5 cm W, 35.6 cm D (17 " × 12 " × 14 ") Weight: 10 kg (22 lb)
References	a) Manufacturer's bulletin No. SB-697 b) Manufacturer's catalog: Operating Instruction Manual for 69-750
Features	
Cost	Gas chromatograph Model 69-750 $1,320.
Remarks	Rotameter Assembly no. 75-300 ($210.) recommended; Constant voltage transformer may be advisable
Address	Gow-Mac Instruments Co. 100 Kings Rd. Madison, NJ 07940 (201) 377-3450

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

H20-PHE
Phenol Analysis
Spectro Products 1
August 1975

Phenol Detector

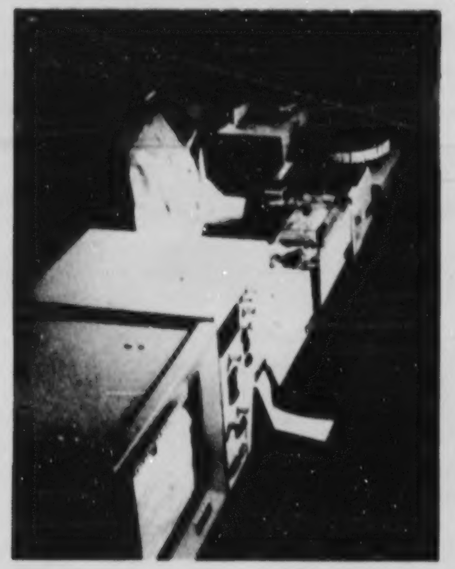
Model PH-2



Class	Laboratory batch sample monitor
Principle of Operation	Ultraviolet differential absorption spectrophotometry utilizing the characteristic wavelength shift of phenols according to pH.
Sensitivity	20 μg/ℓ at 1% absorption - 10 cm cell 100 μg/ℓ at 1% absorption - 2 cm cell
Range	Less than 5.0 μg/ℓ to greater than 20 mg/ℓ. Includes para substituted phenol compounds
Interferences	Compounds absorbing more at pH 4 than at pH 12 at 290 nm, phenol decomposing bacteria, reducing substances, and strongly alkaline conditions of the sample. Also, metal and solids in suspension that may produce strong to slight turbidity when specimen is made basic.
Multiparameter Capability	None
Sampling	ASTM D1783, Section 8; 50 ml required (may have to be distilled)
Performance	Accuracy: Depends upon phenolic standard and sample Reproducibility: 30% relative standard deviation @ 5 μg/ℓ; 1% @ > 100 μg/ℓ Linearity: Less than 1% deviation Noise: 0.3% full scale with minimum damping Sampling time: 4 min. approx. Zero drift: Less than 0.1% full scale per sample cycle after 20 min. warmup Span drift: Less than 0.2% full scale per sample cycle after 20 min. warmup
Requirements	Reagents: Sodium hydroxide, 4 molar solution (NAOH), Phenol free. Water, ASTM D1193, filtered through activated charcoal. Hydrochloric acid, 10% (HCL). Phenol standard (C_6H_5OH), 1.00 g, dissolved in liter of water. Power: 115 V, 50/60 Hz; 60W maximum Size: 38 cmH, 51 cm W, 38 cmD (15" x 20" x 15") Weight: 18 Kg (40 lbs)
References	J. E. Fountaine, P. B. Joshipura, P. N. Keliher, and J. D. Johnson, Anal. Chem. 46, 62 (1974). Manufacturer's specification sheet.

Features	Output: For digital voltmeter 0-1 V or for recorder 0-10 mV Automatic gain control to maintain constant reference lamp intensity 10x scale expansion
Cost	Model PH-2 $3,375
Remarks	If the 50 ml sample turbidity changes excessively when reagents are added, distillation is required. Distillation required for Standard Method.
Address	Spectro Products, Inc. 385 State Street North Haven, Connecticut 06473 (203) 281-0122

Automatic Phenol Monitor
Technicon AutoAnalyzer II



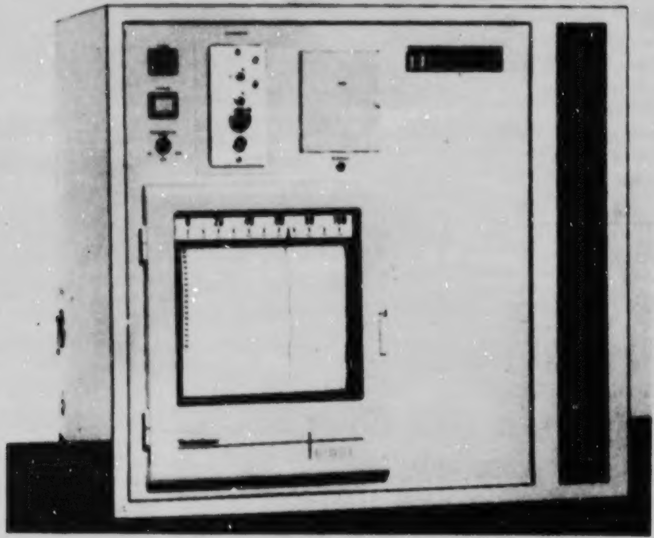
Class	Laboratory batch
Categories of Water	Fresh, Saline, Waste
Principle of Operation	Colorimetric. Samples are aspirated into a sampling line, segmented by air bubbles, distilled, and mixed with the 4-AAP reagent stream. The resulting colored product is measured photometrically and recorded.
Minimum Detectable Sensitivity	2 µg/ℓ
Interferences	Bacteria, Oxidants
Multiparameter Capability	With appropriate modifications: Ammonia, Nitrate + Nitrate, Nitrite, Ortho-Phosphate, Total Inorganic Phosphate, Silicate, Total Soluble Iron, Sulfide, Hexavalent Chromium, Copper, Sucrose, COD, Cyanide, Fluoride, Hardness, Sulfate, Alkalinity (pH 3 min), Alkalinity (pH 8 min), Chloride, Total Kjeldahl Nitrogen, Total Phosphorus
Sampling	Method: Batch Maximum Temperature Input: 29°C Rate: 40/hr (one sample tray)
Performance	Reproducibility: @ 100 µg/ℓ; rel. std. dev. ≈ 1.3% Response Time: 15 minutes Zero Drift: Self-compensated Span Drift: Self-compensated
Operation	Ambient Temperature Range: 13°C - 29°C Temperature Compensation: Self-compensating Relative Humidity Range: 10 - 80% Calibration: Automatic, periodically, with blank (zero) and standard solutions Procedure: Automatic Unattended Period: 1 hr maximum Maintenance: Change reagents as needed

H20-PHE
Phenol Analysis
Technicon 1
August 1975

Requirements	Power: 117 Vac, 50 to 60 Hz; 1.5 KW Weight: 70 Kg (150 lbs) maximum Dimensions: 62 cm × 245 cm bench top (2' × 8') Modules: Sampler IV, Proportioning Pump III, Manifold, Colorimeter, Distillation Apparatus, Digital Printer, Recorder	
Features	Output: Recorder and digital printer Training: Free at Tarrytown, N.Y.	
References	Manufacturer's bulletin "AutoAnalyzer II" and "Industrial Methods 127-71W and 352-74W". Methods for Chemical Analysis of Water and Wastes, EPA-625-16-74-003, U.S. Environmental Protection Agency, Washington, D.C. 20460	
Cost	AutoAnalyzer II for official EPA method (including printer)	$17,640
Remarks		
Address	Technicon Instruments Corp. Tarrytown, N. Y. 10591 (914) 631-8000	

H2O-PHE
Field
Technicon 2
September 1975

Automatic Phenol Monitor
Technicon Monitor IV



Class	Continuous
Categories of Water	Waste
Principle of Operation	Colorimetric, continuous flow. One sample stream is aspirated, mixed with reagents, distilled, color developed with 4-AAP and measured photometrically at 505 nm.
Minimum Detectable Sensitivity	4 µg/ml
Interferences	
Multiparameter Capability	Ammonia, Nitrate + Nitrite, Nitrite, Ortho-Phosphate, Total Inorganic Phosphate, Silicate, Total Soluble Iron, Sulfide (seawater), Hexavalent Chromium, Copper, and Sucrose
Sampling	Method: Continuous Rate: 2 ml/min Maximum Temperature Input: Ambient conditions Filter: Optional Maximum Number of Sample Sources: One (standard); up to 10 with optional equipment
Performance	Accuracy: Rel. Std. Dev. @ 160 µg/ℓ = 0.3% Reproducibility: ±1% of full scale Linearity: 100% Noise: Less than ±0.5% of full scale Response Time: 15 minutes Zero Drift: Effectively zero, automatically compensated Span Drift: ±0.025% of reading per degree temperature change

Operation

Ambient Temperature Range: 13°C to 29°C
Temperature Compensation: Self-correcting upon restandardization
Relative Humidity Range: 10% to 80%
Calibration: Automatic; at selected intervals between 2-24 hours, either a wash solution (zero reading) or a standard solution are run through the analyzer. Any adjustment is done automatically.
Procedure: Automatic
Unattended Period: Approximately 1 week
Maintenance: Change reagents
Reagents: Phosporic Acid, 4-Aminoantipyrine, Potassium Ferricyanide, Hydrochloric Acid, Boric Acid, Sodium Hydroxide, Brij-35™, Distilled Water

Requirements

Power: 110-120 Vac; 60 Hz; 5A maximum
Weight: 63.4 kg (140 lb)
Dimensions: 57.1 cm H × 62.9 cm W × 47 cm D (22½" × 24¾" × 18½")

Features

Output: 0-60 mV for recorder; 0-5 Vdc for telemetry or control
Training: Free to employee of purchaser at Tarrytown, N.Y.
Options: Continuous filter-sampler $

References

(1) Manufacturer's bulletin "Technicon Monitor IV" 1971
(2) Technicon "Industrial Method" No. 356-75 WM
(3) "A Continuous Distillation Technique for On-Line Analysis of Low-Level Phenol in Wastewater", R. Pirritano and H. Marcus, Technicon

Cost

Monitor IV for phenol $9,125 (approx)

Remarks

Stream sampled must be filtered

Address

Technicon Instruments Corporation
Tarrytown, N. Y. 10591
(914)631-8000

PHENOLICS

AUTOMATED 4-AAP METHOD WITH DISTILLATION

(U.S. Environmental Protection Agency)

STORET NO: 32730

1. Scope and Application

1.1 This method is applicable to the analysis of drinking waters, surface waters, saline waters, domestic and industrial wastes.

1.2 The method is capable of measuring phenolic materials from 2 to 500 μg/l in the aqueous phase using phenol as a standard; working ranges are 2 to 200 μg/l and 10 to 500 μg/l.

2. Summary of Method

This automated method is based on the distillation of phenol and subsequent reaction of the distillate with alkaline ferricyanide and 4-aminoantipyrine to form a red complex which is measured at 505 or 520 nm. The same manifold is used with the AAI or AAII.

3. Sample Handling and Preservation

3.1 Biological degradation is inhibited by the addition of 1 g/l of copper sulfate to the sample and acidification to a pH of less than 4 with phosphoric acid. The sample should be kept cold (5 - 10°C) and should be analyzed within 24 hours after collection.

4. Interference

4.1 Interferences from sulfur compounds are eliminated by acidifying the sample to a pH of less than 4.0 with H_3PO_4 and aerating briefly by stirring and adding $CuSO_4$.

4.2 Oxidizing agents, such as chlorine as detected by the liberation of iodine upon acidification in the presence of potassium iodide, are removed immediately after sampling by the addition of an excess of ferrous ammonium sulfate. (6.5) If chlorine is not removed, the phenolic compound will be partially oxidized and the results will be low.

4.3 Background contamination from plastic tubing and sample containers is eliminated by filling the wash receptacle by siphon (using Kel-f tubing) and using glass tubes for the samples and standards.

5. Apparatus

5.1 Technicon AutoAnalyzer (I or II)

- 5.1.1 Sampler
- 5.1.2 Manifold
- 5.1.3 Proportioning pump II or III
- 5.1.4 Heating bath with distillation coil
- 5.1.5 Distillation head
- 5.1.6 Colorimeter equipped with a 50 mm flow cell and 505 or 520 nm filter
- 5.1.7 Recorder

6. Reagents

6.1 Distillation Reagent: Add 100.0 ml of conc. phosphoric acid (85% H_3PO_4) to 800 ml of distilled water, cool and dilute to 1 liter.

6.2 Buffered Potassium Ferricyanide: Dissolve 2.00 g potassium ferricyanide, 3.10 g boric acid and 3.75 g potassium chloride in 800 ml of distilled water. Adjust to pH of 10[illegible] with 1 N sodium hydroxide and dilute to 1 liter. Add 0.5 ml of Brij-35.

6.3 Sodium Hydroxide (1 N): Dissolve 40.0 g NaOH in 500 ml of distilled water, cool and dilute to 1 liter.

6.4 4-Aminoantipyrine: Dissolve 0.65 g of 4-aminoantipyrine in 800 ml of distilled water and dilute to 1 liter.

6.5 Ferrous Ammonium Sulfate: Dissolve 1.1 g ferrous ammonium sulfate in 500 ml distilled water containing 1 ml H_2SO_4 and dilute to 1 liter with freshly boiled and cooled distilled water.

6.6 Stock Phenol: Dissolve 1.00 g phenol in 500 ml of distilled water and dilute to 1.0 liter. Add 1.0 g $CuSO_4$ and 0.5 ml conc. H_3PO_4 as preservative. 1.0 ml = 1.0 mg phenol

6.7 Standard Phenol Solution A: Dilute 10.0 ml of stock phenol solution (6.6) to 1 liter.

Preserve by adding 0.1 g $CuSO_4$ and 2 drops of conc. H_3PO_4. 1.0 ml = 0.01 mg phenol.

6.8 Standard Phenol Solution B: Dilute 100.0 ml of standard phenol solution A (6.7) to 1.0 liter with distilled water. Preserve by adding 0.1 g $CuSO_4$ and 2 drops of conc. H_3PO_4. 1.0 ml = 0.001 mg phenol.

6.9 Standard Solution C: Dilute 100.0 ml of standard phenol solution B (6.8) to 1.0 liter with distilled water. Preserve by adding 0.1 g $CuSO_4$ and 2 drops of conc. H_3PO_4. 1.0 ml = 0.0001 mg phenol.

6.10 Using a standard solution A, B or C prepare the following standards in 100 ml volumetric flasks. Each standard should be preserved by adding 0.1 g $CuSO_4$ and 2 drops of conc. H_3PO_4 to 100 ml.

ml of Standard Solution	Conc. µg/l
Solution C	
1.0	1.0
2.0	2.0
3.0	3.0
5.0	5.0
Solution B	
1.0	10.0
2.0	20.0
5.0	50.0
10.0	100.0
Solution A	
2.0	200.0
3.0	300.0
5.0	500.0

7. Procedure

7.1 Set up the manifold as shown in Figures 1 and 2.

7.2 Fill the wash receptacle by siphon. Use Kel-F tubing with a fast flow (1 liter/hr.).

7.3 Allow colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Use polyethylene tubing for sample line. When new tubing is used, about 2 hours may be required to obtain a stable baseline. This two hour time period may be necessary to remove the residual phenol from the tubing.

7.4 Place appropriate phenol standards in sampler in order of decreasing concentration. Complete loading of sampler tray with unknown samples, using glass tubes.

NOTE 1: If samples have not been preserved as instructed in 3.1, add 0.1 g $CuSO_4$ and 2 drops of conc. H_3PO_4 to 100 ml of sample.

8. Calculation

8.1 Prepare standard curve by plotting peak heights of standards against concentration values. Compute concentration of samples by comparing sample peak heights with standards.

9. Precision and Accuracy

9.1 In a single laboratory (MDQARL), using sewage samples at concentrations of 3.8 15, 43 and 89 µg/l, the standard deviations were ±0.5, ±0.6, and ±1.0, respectively. At concentrations of 73, 146, 299 and 447 the standard deviations were ±1.0, ±1.8, ±4.2 and ±5.3 µg/l, respectively.

9.2 In a single laboratory (MDQARL), using sewage samples at concentrations of 5.3 and 82 µg/l, the recoveries were 78% and 98%. At concentrations 168 and 489 µg/l, the recoveries were 97% and 98% respectively.

BIBLIOGRAPHY

1. Technicon AutoAnalyzer II Methodology, Industrial Method No. 127-71W, AAII.

2. Standard Methods for the Examination of Water and Wastewater, 13th edition, American Public Health Association, Inc., New York, NY (1971).

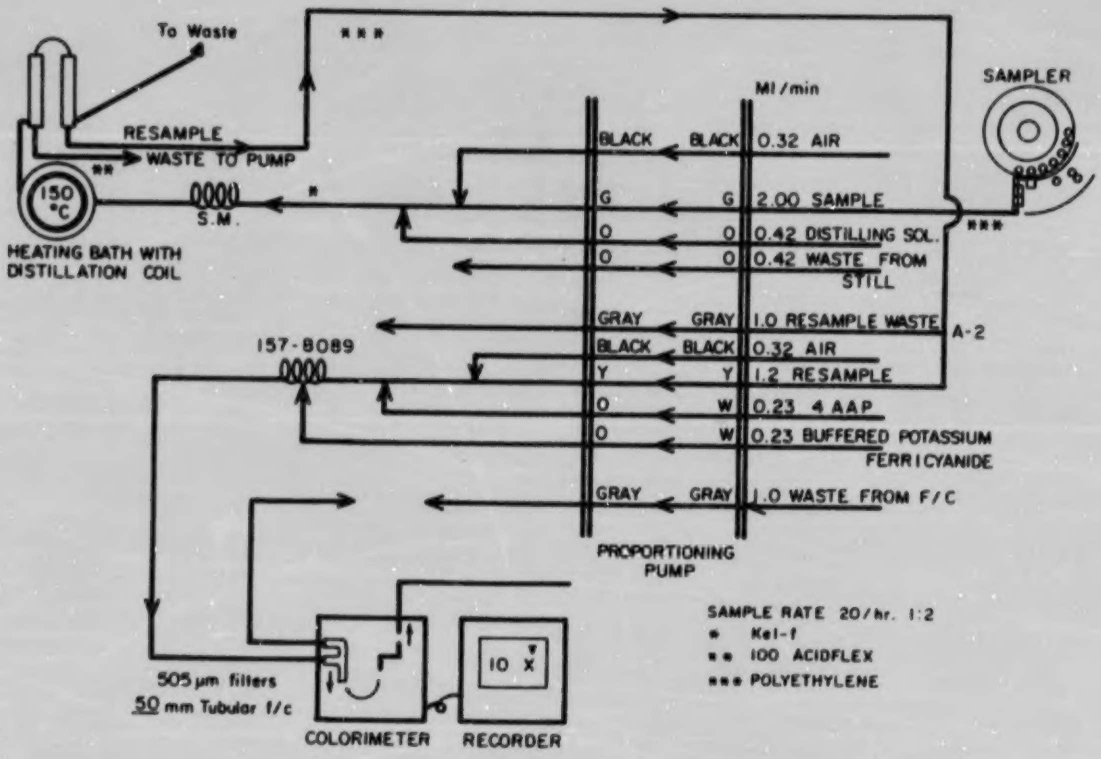
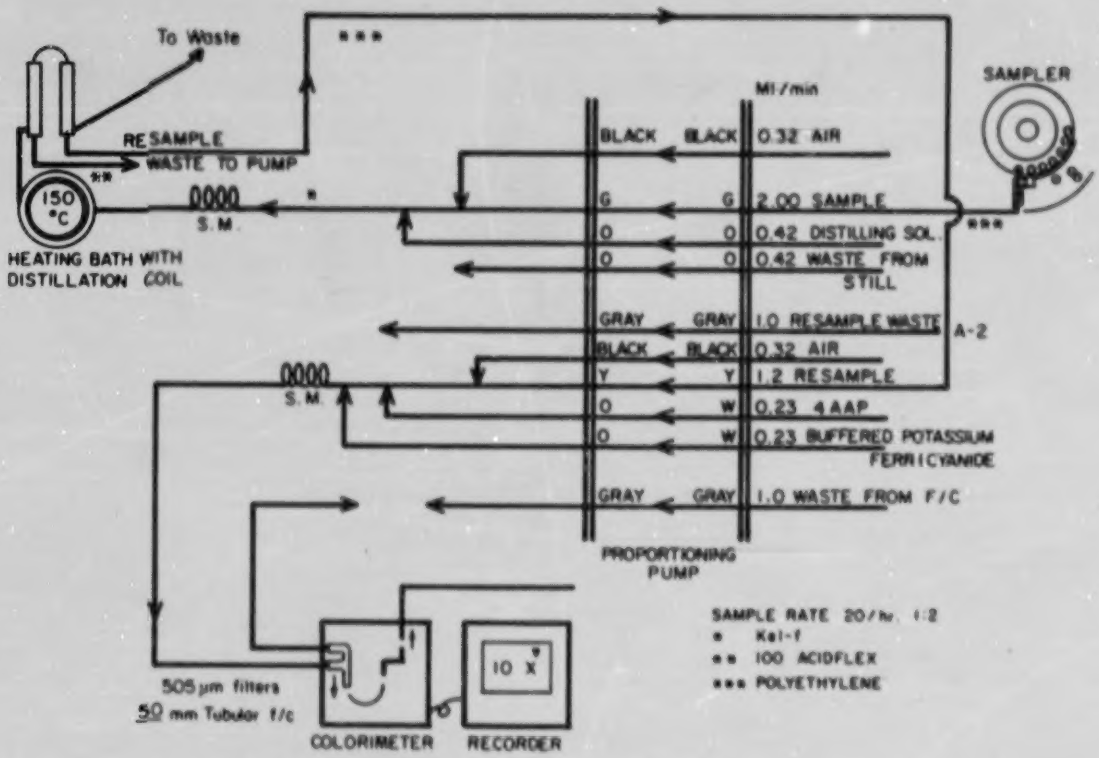

To Waste
***
RESAMPLE
WASTE TO PUMP
**
150 °C
*
S.M.
HEATING BATH WITH
DISTILLATION COIL
Ml/min
SAMPLER
BLACK
BLACK
0.32 AIR
G
G
2.00 SAMPLE
O
O
0.42 DISTILLING SOL.
O
O
0.42 WASTE FROM STILL
***
GRAY
GRAY
1.0 RESAMPLE WASTE
A-2
157-8089
BLACK
BLACK
0.32 AIR
Y
Y
1.2 RESAMPLE
O
W
0.23 4 AAP
O
W
0.23 BUFFERED POTASSIUM FERRICYANIDE
GRAY
GRAY
1.0 WASTE FROM F/C
PROPORTIONING PUMP
SAMPLE RATE 20/hr. 1:2
* Kel-f
** 100 ACIDFLEX
*** POLYETHYLENE
10 X
505 μm filters
50 mm Tubular f/c
COLORIMETER
RECORDER

Figure 1. Phenol Auto Analyzer II.


To Waste
***
RESAMPLE
WASTE TO PUMP
**
150 °C
0000
S.M.
*
HEATING BATH WITH
DISTILLATION COIL
Ml/min
SAMPLER
BLACK
BLACK
0.32 AIR
G
G
2.00 SAMPLE
***
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O
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O
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0.42 WASTE FROM STILL
GRAY
GRAY
1.0 RESAMPLE WASTE
A-2
BLACK
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S.M.
O
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0.23 4 AAP
O
W
0.23 BUFFERED POTASSIUM FERRICYANIDE
GRAY
GRAY
1.0 WASTE FROM F/C
PROPORTIONING PUMP
SAMPLE RATE 20/hr. 1:2
* Kel-f
** 100 ACIDFLEX
*** POLYETHYLENE
505 µm filters
50 mm Tubular f/c
10 X
COLORIMETER
RECORDER

Figure 2. Phenol Auto Analyzer I .

**Petrochemicals
PET**

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FOR
PETROCHEMICALS IN WATER

Mnemonic

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Appendix

A. INTRODUCTION

Serious contamination of water resources is one hazard associated with a large and expanding petrochemical industry (Ref. 1). As the name implies, petrochemicals are chemical substances produced commercially from petroleum or natural gas. In general, petrochemicals are relatively pure organic compounds which serve as the basic building blocks for a host of synthetic organic products. Organic polymers account for the greatest utilization of petrochemicals. Familiar examples include synthetic rubber, vinyl, polystyrene, polyethylene, polyurethane, nylon, polyester, epoxy, and acrylic. Petrochemicals are also used in pesticide, drug, and dye manufacture as well as industrial solvents. Ordinarily, the term does not include hydrocarbon fuels and lubricants, nor chemicals produced by others than the processor handling the petroleum raw material (Ref. 2). Insofar as this discussion is concerned, any water contamination related to the manufacture or use of petrochemicals (such as in subsequent chemical manufacturing) is considered relevant. This definition covers literally thousands of organic compounds.

1. Background

Except for carbon black made from natural gas, there were no petrochemicals prior to the production of isopropyl alcohol in 1920 (Ref. 2). Since then the growth of the petrochemicals has been spectacular, particularly the aliphatic (non-benzenoid) organics which now comprise the bulk of production. Petroleum or natural gas are now the source for a number of commercial organics once derived entirely from other sources. Examples include:

acetone -- originally from wood-distillation

ethyl chloride -- once made from fermentation alcohol

butadiene (synthetic rubber monomer) -- also made from fermentation alcohol during World Wars I and II.

Other petrochemicals are still being produced from other sources. Examples include:

benzene and acetylene -- coal

glycerine -- animal fats

ethanol -- carbohydrate fermentation

The most significant development has been the advent of the giant integrated manufacturing complexes such as those located in Puerto Rico (Ref. 1, 3). These complexes are

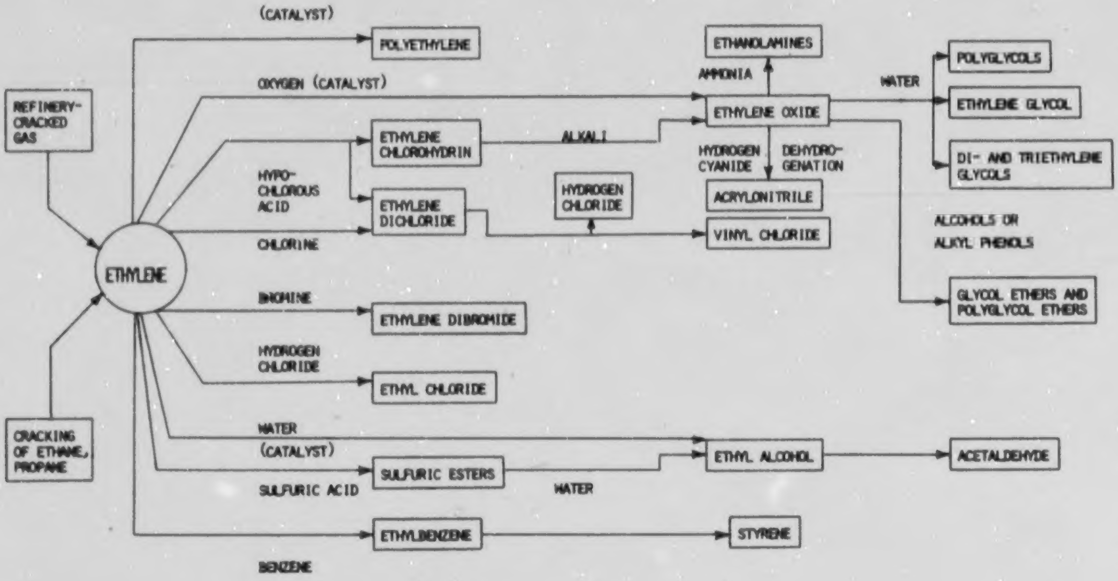
(CATALYST)
POLYETHYLENE
OXYGEN (CATALYST)
REFINERY-CRACKED GAS
ETHYLENE CHLOROHYDRIN
ALKALI
HYPO-CHLOROUS ACID
ETHYLENE DICHLORIDE
HYDROGEN CHLORIDE
CHLORINE
ETHYLENE
BROMINE
ETHYLENE DIBROMIDE
HYDROGEN CHLORIDE
ETHYL CHLORIDE
WATER
(CATALYST)
SULFURIC ESTERS
SULFURIC ACID
WATER
ETHYLBENZENE
BENZENE
STYRENE
CRACKING OF ETHANE, PROPANE
ETHANOLAMINES
AMMONIA
ETHYLENE OXIDE
HYDROGEN CYANIDE
DEHYDRO-GENATION
ACRYLONITRILE
VINYL CHLORIDE
ETHYL ALCOHOL
ACETALDEHYDE
WATER
POLYGLYCOLS
ETHYLENE GLYCOL
DI- AND TRIETHYLENE GLYCOLS
ALCOHOLS OR ALKYL PHENOLS
GLYCOL ETHERS AND POLYGLYCOL ETHERS

FIGURE A-1. Petrochemicals from ethylene (from Ref. 2).

Table A-1.

U.S. Petrochemical Production in 1973 (from Ref. 4)

Petrochemical	Production Billions of Pounds 1973	% Annual Change		H_2O Soluble, > 10% (from Ref. 7, 10)
		1972-73	1963-73	
Ethylene	22.41	7.4	11.5	–
Benzene	10.65	16.1	8.4	–
Propylene	8.76	3.4	12.4	–
Ethylene dichloride	7.90	- 8.1	16.0	–
Methanol, synthetic	7.12	19.5	11.8	+
Toluene	6.78	2.2	8.7	–
Ethylbenzene	6.50[a]	1.2	10.2	–
Formaldehyde, 37%	6.17	9.3	9.3	+
Styrene	6.01	1.1	10.8	–
Vinyl chloride	5.35	3.3	14.1	–
Ethylene oxide	3.88	- 1.9	7.5	+
Butadiene	3.66	3.9	4.7	–
Ethylene glycol	3.29	- 0.3	7.1	+
Dimethyl terephthalate	2.69[a]	30.9	23.7	–
Cumene	2.67	-12.0	19.9	–
Terephthalic acid	2.49[a]	23.6	--	–
Acetic acid	2.42	12.5	8.9	+
Cyclohexane	2.35	3.0	8.1	–
p-Xylene	2.32	5.2	24.3	–
Phenol, total	2.25	12.7	9.2	–
Acetone	1.99	13.0	7.7	+
Ethanol, synthetic	1.97[a]	5.1	0.1	+
Isopropanol	1.76	- 5.1	1.8	+
Propylene oxide	1.75	15.9	13.4	–
Acetic anhydride	1.55	- 0.6	2.0	+
Vinyl acetate	1.48	23.2	12.9	–
Acetaldehyde	1.40[a]	7.7	2.0	+
Acrylonitrile	1.35	21.3	11.5	–

[a] Estimate

based on a large central petrochemical plant which supplies feedstocks to satellite manufacturing plants. The environmental impact of a Puerto Rico petrochemical complex is the subject of an extensive report (Ref. 1) by the U.S. Environmental Protection Agency (EPA).

By the end of the 1960's petrochemical plants with an annual production of over 100,000 metric tons had become commonplace (Ref. 3). Process obsolescence had become a contending factor. For example, ethylene processes have displaced acetylene processes in the production of vinyl chloride monomer and vinyl acetate (Ref. 3). Current domestic production of petrochemicals is shown in Table A-1. The largest volume petrochemical is ethylene. Figure A-1 shows the variety of petrochemicals derived from ethylene.

2. Characteristics

In some cases petrochemical contamination of water resources is minimized by the combined insolubility and volatility of the specific organic(s) involved. In these circumstances air pollution may be a more serious consequence than water pollution. However, when waste from the manufacture and use of petrochemicals does penetrate water resources, several problems may arise. For example, present drinking water treatment plants which emphasize sedimentation, aeration, filtration, and chlorination may be poorly equipped to remove petrochemical contaminants completely. Since we generally ingest about 1 liter (≈ 1 quart) of water each day, drinking water purification processes which transmit ng/l to mg/l concentrations of toxic organic chemicals risk exposure of the public to health hazards (Ref. 5).

If the hazards of a petrochemical are to be assessed properly, it is necessary to establish threshold levels below which no adverse effects are observed (Ref. 5). There are many difficulties in relating a particular public health problem with a petrochemical contaminant. Often the appropriate human toxicity data is unavailable and animal toxicity studies must be used for comparison instead. Precise comparisons are not always possible. Also, trace amounts of a variety of petrochemicals frequently contaminate water resources in industrial areas. The combined effects of these and other substances may be more than simply additive. Consequently the entire complex of environmental and physiological interrelationships of the particular pollutants must be taken into consideration.

Petrochemical contaminants occur in water in a diversity of chemical types. The fact that they are organic virtually assures the eventual dissimilation of even the most resistant petrochemicals by microbial biota. These processes would be expected to vary from substance to substance and microbe, but much remains to be learned (Ref. 5). Aquatic accumulations of organic chemical substances not directly toxic may, nevertheless, create a biochemical oxygen demand (BOD) which can adversely affect fish and other aquatic life. Other hazards include inhibition or contamination of aquatic food production.

Petrochemicals and their derived products encompass such a large number of compounds that it will not be possible here to discuss each in terms of its individual pollution potential. For this the reader is referred to several texts which contain toxicity data on a large number of organic compounds (Refs. 5-8). Water Quality Criteria Data Book, Volume 1 (Ref. 5) published by the EPA is the most recent compilation of data associated with water pollution hazards from organic substances. Data from the literature is tabulated under the following titles:

I. Concentration of Organic Pollutants Looked For and Found in Fresh Water

II. Mammalian Acute and Chronic Toxicity of Organic Pollutants Found in Fresh Water

III. Mammalian Acute and Chronic Toxicity of Potential Organic Pollutants of Fresh Water

IV. Concentration and Effects of Organic Pollutants in Human and Animal Tissue

V. Carcinogenicity in Mammals or Organic Pollutants Found in Fresh Water Examined by the Oral Route of Administration

Va. Carcinogenicity in Mammals of Organic Pollutants Found in Fresh Water Examined Only by Routes of Administration Other Than Oral

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VIa. Carcinogenicity in Mammals of Potential Organic Pollutants of Fresh Water Examined Only by Routes of Administration Other Than Oral

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X. Sources of Potential Organic Pollutants of Fresh Water

XI. Reported Maximum Concentration of Organic Chemicals Found in Fresh Water Producing No Effect in Mammals When Administered on a Chronic Basis or Tested for Organoleptic Effects in Man

XII. Acute Toxicity Ranking of Organic Chemicals Found in Fresh Water as Determined by LD_{50} in Mammals Using Oral Administration

XIII. Acute Toxicity Ranking of Potential Organic Pollutants of Water as Determined by LD_{50} in Mammals Using Oral Administration

XIV. Ranking of Reported Threshold Doses Obtained by Chronic Administration in Rats

Discussion of the toxic potential of selected individual organic pollutants can be found in a predecessor publication, Water Quality Criteria, second edition (Ref. 6) by McKee and Wolf, published by the California Water Resources Board. Other discussions of the toxicity of many individual organics may be found in The Merck Index, 8th edition (Ref. 7). The most extensive compilation of toxicity data is found in the Toxic Substances List, 1973 edition (Ref. 8), published by the U.S. Department of Health, Education and Welfare (DHEW). Over 25,000 substances are listed; most of these are organic. Although Refs. 7 and 8 are not directed primarily to the subject of water pollution, they are useful sources of toxicity information.

Because petrochemicals and related products include so many different organic compounds, the discussion here will be limited to examples from the major organic classes to illustrate water quality hazards. Special cases such as "Pesticides" and "Phenols" are discussed under those titles in separate sections (see H2O-PES and H2O-PHE). Problems associated with petroleum are discussed under "Oil and Grease" (H2O-OIL).

3. Chemical Classification

Organic chemical compounds are customarily classified according to their reactive functional groups. These functional groups are incorporated into the carbon skeleton of the molecule and they play a major role in determining the chemical reactivity of the particular organic compound. Petrochemicals can be produced in virtually every conceivable class of chemical functionality. Wastes from the manufacture and use of petrochemicals also can contain a number of by-products. The chemical identity of many of these may or may not be well defined. Thus, the potential for petrochemical pollution encompasses a diverse variety of organic chemical types and thousands of individual compounds.

4. Hydrocarbons

Hydrocarbons comprise a huge family of known organic compounds composed entirely of carbon (C) and hydrogen (H). Except for methane (CH_4), hydrocarbon compounds consist of carbon atoms bonded together in chains, branched chains, rings or combinations of these. This linkage of carbons forms the molecular skeletal structure of a hydrocarbon compound.

Each carbon is tetravalent, i.e., it has four bonding electrons. Thus, a particular carbon atom can be bonded to four other carbons, although this is infrequent with the known hydrocarbons. Most often, a carbon atom is bonded to two other carbons as part of a chain or ring. A carbon at a branch point or juncture of rings is bonded to three other carbons. The remaining bonding capacity of the carbons can be satisfied by bonding with hydrogen. Since hydrogen has only one bonding electron, each hydrogen forms only one single bond with carbon.

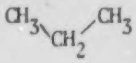
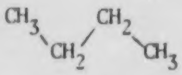
When a hydrocarbon molecule contains carbon atoms which are bonded to less than four carbon and/or hydrogen atoms, the residual bonding requirements (valences) may be satisfied by double or triple bonds between two carbons. Since molecular hydrogen (H_2) can be added across each multiple bond, the molecule is considered to have less than its full capacity of hydrogen, i.e., it is unsaturated. These doubly or triply bonded carbons have a chemical reactivity different from the relatively inert fully saturated carbons. For this reason hydrocarbons having different types of bonds are classified in separate chemical categories.

4.1 Alkanes

Alkanes are fully saturated acyclic hydrocarbons having the general formula C_nH_{2n+2}. They make up the bulk of petroleum and natural gas used as the basic raw material (feedstock) for the petrochemicals industry. Alkanes having one to four carbons (C_1 - C_4) are gases (Table A-3). Large quantities of these are produced in relatively pure form to serve as petrochemical intermediates. What is not used in this manner as petrochemical feedstock is used or sold as fuel. Refinable alkanes above C_4 are liquids used for fuels and lubricants. They also may be broken down (cracked) into smaller molecules for petrochemical feedstocks and fuels.

Table A-2

Alkane Gases Used for Petrochemical Feedstock

Name	Molecular Structure	Solubility in H_2O g/l at 17°C, 1 atm[a]
Methane	CH_4	0.03
Ethane	CH_3-CH_3	0.06
Propane		0.12
Butane		0.4

[a] Calculated from data in Ref. 7.

All alkanes, whether gases, oily liquids or waxy semisolids are extremely insoluble in water. Methane (marsh gas) produced by natural fermentation processes, is a good example (see Table A-2). Chemically, alkanes are relatively inert. As such, the non-volatile (higher molecular weight) alkanes are familiar in the household as mineral oil and petroleum jelly.

Aside from explosions and fires, the principle hazard associated with alkanes is a physical interference with biological and environmental processes. Gaseous alkanes (C_1 - C_4) may dilute or displace the more desirable normal gases in biosystems. These alkane gases are not sufficiently soluble in water (Table A-2) to have any significant toxic effects on humans as a result of ingestion.

Liquid alkanes may produce a film on water surfaces or coat breathing organs of aquatic biota which interferes with normal gas exchange. The volatile liquid alkanes (C_5 - C_9) may act as fat disolving solvent and thus disrupt normal life processes. Neurological functions in humans may be impaired with large doese (e.g., narcosis), but this would involve the unlikely ingestion of distasteful, visibly oily water.

Toxicity data for individual alkanes (apart from petroleum) toward aquatic life is very sparse and perhaps misleading. McKee and Wolf (Ref. 6) list an example of *n*-heptane as being lethal to fish (white roach) at 30 mg/l at 21°C in 1 to 4 hours. Whereas, in another example, the 96 hour TL_m for mosquito fish in turbid water at 20-27°C was 4924 mg/l? Since this is about 100 times the solubility of heptane at these temperatures (ca. 50 mg/l), clearly the fish were not actually being exposed to such concentrations in solution. Further aquatic toxicity data on individual alkanes is not available from published sources.

4.2 Cycloalkanes

Cycloalkanes are very similar to the alkanes except that they have rings. This alters their general formula to C_nH_{2n}, C_nH_{2n-2}, C_nH_{2n-4}, ... , depending on whether 1, 2, 3 or more rings are present. They have no multiple carbon-carbon bonds, therefore they do not possess the chemical reactivity associated with unsaturated hydrocarbons. Cycloalkanes are found in petroleum where they are also known as naphthenes. Generally they are various derivatives of cyclohexane, a saturated 6-membered ring, C_6H_{12}. Each naphthene differs according to the saturated hydrocarbon (alkyl) substituents attached to the cyclohexane ring. Naphthenes are used as petrochemical feedstock. Cyclohexane itself is produced directly from benzene.

Gaseous cycloalkanes are rare. The environmental effects of the liquid and waxy cycloalkanes are analogous to those of the alkanes. McKee and Wolf (Ref. 6) list two contradictory examples. In one report, 10 mg/l of cyclohexane in water was lethal to fish in four hours; methyl cyclohexane was 5 times less toxic. Another study reported the 96-hour TL_m of cyclohexane to be 15,000 mg/l for mosquito fish. As with the data for heptane (section 4.1) this value exceeds the solubility of cyclohexane in water by a factor of at least 100. The validity of this TL_m value is doubtful. No other aquatic toxicity data could be found for cycloaklanes.

4.3 Alkenes

Alkenes (olefins) are unsaturated, acyclic hydrocarbons characterized by one or more carbon-carbon double bonds. They have the general formula C_nH_{2n}, C_nH_{2n-2}, . . . , depending on whether 1, 2, or more double bonds are present. Unlike alkanes and cycloalkanes, the simple alkenes (ethylene, propylene) are not found in natural hydrocarbon deposits in significant quantities. Nevertheless, they are a most important class of commercial organic chemicals. They are produced from the dehydrogenation and cracking of alkanes. Alkenes now account for a predominant part of the petrochemical industry (see Table A-1). Most of the alkene production goes into feedstock for the production of other organic chemicals (monomers) and polymers.

The alkene, ethylene ($CH_2 = CH_2$), is the largest volume petrochemical (Ref. 4). It can occur to a small extent ($< 4\%$) in illuminating gas (Ref. 7), otherwise it is produced from alkanes. As indicated in Figure A-1, ethylene is the intermediate petrochemical for a host of petrochemical products.

Ethylene plays an important role biologically in the natural and artificial ripening of fruit (Ref. 6,7). Apparently it is more toxic in water than its alkane counterpart, ethane. McKee and Wolf (Ref. 6) list lethal concentrations (LC) for ethylene at around 25 mg/l in 1 hour for sunfish from two different studies.

Reference 5 lists propylene, isobutylene and isoprene (2-methyl-1,3-butadiene) as other potential alkene pollutants in water but cite no further toxicity data for aquatic life. Isoprene, used in making synthetic rubber, imparts a discernible odor to water at 5 µg/l (Ref. 6).

Higher molecular weight alkenes, the so-called α-olefins, are important in the manufacture of synthetic detergents. In the aquatic environment they would be expected to have an impact comparable to the alkanes of the same molecular weight range (kerosine).

4.4 Cycloalkenes

Cycloalkenes are widespread in nature, being produced by most plants. The most abundant of these are the terpenes ($C_{10}H_{16}$) which are produced in large amounts by conifers. A familiar example is turpentine distilled from the exudate of Southern Slash Pine.

Strictly as petrochemicals, cycloalkenes are not so prominent. Cyclopentadiene is an important petrochemical intermediate in the synthesis of several cyclic chlorinated chyrocarbon pesticides (e.g., dieldrin, aldrin, endrin) but no aquatic toxicity data is available. Cyclohexene appears to be slightly more toxic than its cycloalkane counterpart, cyclohexane (Ref. 6).

4.5 Alkynes

Alkynes are hydrocarbons which have at least one doubly unsaturated bond between adjacent carbons. These two unsaturated bonds plus the usual bond linking the two carbons is known as a triple bond ($C \equiv C$). Alkynes have the general formula C_nH_{2n-2}, C_nH_{2n-6}, . . ., depending on whether 1, 2, or more triple bonds are present.

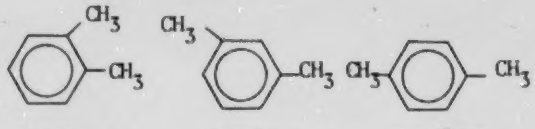
Acetylene ($HC \equiv CH$) is the most important alkyne petrochemical. At one time it surpassed ethylene in production and use. Acetylene is one of the most soluble hydrocarbon gases in water (ca. 1 g/l, 18°C). McKee and Wolf (Ref. 6) list lethal concentrations of 0.2 g/l for brook trout and 0.4 g/l for goldfish during ca. 1-1/2 days. Other studies cited required about 10 times these concentrations for fingerling salmon and young brook trout.

4.6 Arenes

The hydrocarbons discussed up to this point, whether saturated or unsaturated, are known as "aliphatic". However, when unsaturated carbon atoms are linked to form one or more 6-membered (benzene) rings, a distinctly different type of hydrocarbon emerges. These benzenoid compounds are known as "aromatic" hydrocarbons or simply "arenes". The chemistry of the aromatics is so different from aliphatic chemistry that it divides organic chemistry into two major subsidisions. Although the term "aromatic hydrocarbon" persists widely, many benzeniod compounds are not odoriferous. The shorter version, "arene", comparable to "alkene", will be employed here.

Arenes differ from one another according to the substitution of ring hydrogens by aliphatic (alkyl) or aromatic (aryl) groups. Benzene (C_6H_6) is the simplest compound of the series. Substitution of an alkyl group (e.g., methyl, ethyl, propyl) for a single hydrogen gives methyl, ethyl or propyl benzene. Methyl benzene is commonly known as toluene. In commerce benzene and toluene are also known as benzol and toluol. However, "benzine" is a European term for naphtha or "white gasoline" (*aliphatic* petroleum distillate) which should not be confused with benzene, an *aromatic* compound.

Multiple alkyl substitution for the hydrogens on the benzene ring at different carbon positions allows different compounds to have the same atomic composition (isomers). Thus dimethyl benzene (xylene) occurs as three different geometric isomers: *ortho*, *meta* or *para* (see Fig. A-2). Generally these are abbreviated: *o*-, *m*-, *p*-xylene. They could also be termed: 1,2- , 1,3- or 1,4-dimethyl benzene. The numbering system is preferred as substitution patterns become more complex.



o-xylene *m*-xylene *p*-xylene

Figure A-2. Xylene isomers.

Benzene may also be substituted by aromatic (aryl) groups. For example, benzene substituted at one C-H bond by another benzene ring (phenyl group, C_6H_5-) is known as biphenyl (C_6H_5-C_6H_5, Figure A-3). Two benzene rings fused to form two adjoining 6-membered rings is known as naphthalene ($C_{10}H_8$, Figure A-4).

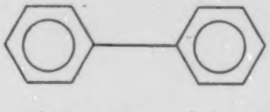


Figure A-3. Biphenyl

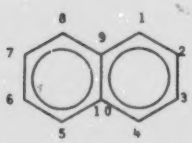


Figure A-4. Naphthalene substitution numbering system.

Arenes are an important class of petrochemicals. Primarily they are intermediates for other petrochemical products. For example, benzene is alkylated with propylene which is then oxidized to phenol plus acetone. Both products are important commercially. *p*-Xylene is oxidized to terephthalic acid, a petrochemical intermediate for polyester fibers. Naphthalene is important in the manufacture of numerous dyes.

In general the aromatic hydrocarbons are more water soluble and more toxic than the alphatics. The solubility of benzene in water is 0.82 g/l at 22°C (Ref. 6), more than 1000 times the minimum threshold of taste or odor. For sunfish 24- and 48-hour TL_m values are 20 mg/l; 24-hour LC_{100} values are ca. 35 mg/l. Toluene and the xylenes show similar behavior.

Naphthalene, though less soluble (30 mg/l, 20°C) than benzene, is more toxic (Ref. 6). For example, 1-hour LC_{100} values are 4-10 mg/l for sunfish. Other species may better tolerate somewhat higher concentrations, but 2-3 mg/l for 3 days is deadly to fingerling salmon. Even lower concentrations (1 mg/l) can taint fish flesh.

5. Halogenated Hydrocarbons

Halogenation of hydrocarbons is the chemical process whereby one or more halogens are incorporated into the hydrocarbon molecule. Among the halogen elements employed as functional groups, chlorine (Cl) is the most widely used, followed by fluorine (F), bromine (Br) and iodine (I). Except for fluorine, the halogen functional groups tend to dominate the chemical and toxicity characteristics of the halogenated hydrocarbons. For this reason separation of the halogenated hydrocarbons into aliphatic and aromatic divisions is less significant than in the preceding section on hydrocarbons.

Fluorine is significantly different from the other halogens. Fluorine atoms are smaller in size and bind very tightly to carbon atoms. This gives them an inertness resembling a methyl group (CH_3-). Small hydrocarbon molecules are fluorinated to form gaseous products such as the Freon refrigerants or tetrafluorethylene (TFE). TFE is polymerized to PTFE, known familiarly as Teflon. In general the gaseous fluorocarbons are as innocuous to the aquatic environment as their hydrocarbon analogs.

On the other hand, chlorinated hydrocarbons which constitute the bulk of halohydrocarbon production pose a variety of problems for the aquatic environment. Chlorinated hydrocarbons are generally less volatile than their hydrocarbon analogs. The simplest, methyl chloride (CH_3-Cl), is a gas used familiarly as a refrigerant spray for athletic injuries. This ether-like gas is soluble in water to 9 g/l at 20°C (Ref. 6), making the water unpalatable. Aquatic toxicity data is lacking. Other chloro-derivatives of methane, methylene chloride (CH_2Cl_2), chloroform ($CHCl_3$) and carbon tetrachloride (CCl_4), are widely used commercial solvents. Acute and chronic aquatic toxicity data (Ref. 6) are sparse on these compounds, although sufficient animal test data are available (Refs. 5-8) to suggest serious concern at any detectable level in drinking water.

A number of two-carbon compounds are produced for a variety of purposes. Trichloroethylene ($ClCH{=}CCl_2$) is a common dry cleaning solvent. Vinyl chloride ($CH_2{=}CHCl$) is an important petrochemical intermediate for polymers which has recently been found to be a serious health hazard (Ref. 9). The fact that it is a gas only slightly soluble in water does not exclude it from concern for the aquatic environment.

Many of the other halogenated hydrocarbons are discussed under Pesticides (H2O-PES). This includes the polychlorinated biphenyls (PCB) which are not used as pesticides but are associated with them environmentally. See Pesticides (H2O-PES) for toxicity and solubility data. Extensive aquatic toxicity data on these pesticides are also presented in Table II of Reference 5.

6. Nitrogenated Hydrocarbons

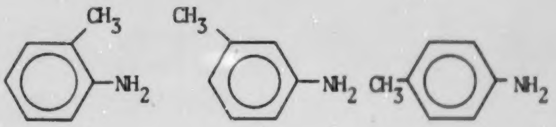
Petrochemicals may also contain nitrogen (N) in addition to C and H. Such organic compounds fall into somewhat disparate categories which are discussed below.

6.1 Amines

Amines are organic derivatives of ammonia (NH_3) in which one or more of the N-H hydrogens is substituted by an alkyl or aryl functional group. Like ammonia, amines are bases, i.e., they can accept hydrogen ions (H^+) or they can donate electron pairs for bonding. Although they are not as strong as the inorganic strong bases (alkalis), they can be extracted from organic solution readily by dilute aqueous mineral acids. In this respect they are unique among organic compounds. This property allows them to be separated from neutral and acidic organic compounds in organic solvents.

Amines may be primary, secondary or tertiary depending on whether one, two or three N-H hydrogens have been replaced by alkyl or aryl groups. Primary aliphatic amines are named according to their alkyl substituents, e.g., methyl amine ($CH_3\text{-}NH_2$), ethyl amine ($CH_3CH_2\text{-}NH_2$). Because of manufacturing convenience secondary and tertiary amines often have the same repeating functional group, e.g., diethyl amine ($CH_3CH_2\text{-}NH\text{-}CH_2CH_3$), triethylamine [$(CH_3CH_2)_3N$].

Aromatic amines can be named similarly. For example, an amine with two phenyl substituents (benzene rings) is simply named diphenylamine ($C_6H_5\text{-}NH\text{-}C_6H_5$). However, the primary aromatic amine derived from one phenyl substituent is not commonly known as phenyl amine but as aniline. When the aryl substituent is a methyl substituted phenyl group (or tolyl group) the amine is known as toluidine. Toluidine occurs in three geometric isomers (see Fig. A-5).



o-toluidine *m*-toluidine *p*-toluidine

Figure A-5. Toluidine isomers.

Amines may also be formed by enclosing the nitrogen in a ring structure, either aliphatic or aromatic. Most of these cyclic amines have individual names. For example, in the saturated 6-membered ring the amine is called piperidine (Fig. A-6); the aromatic 6-membered ring amine is known as pyridine (Fig. A-7). Rules of nomenclature for other N-heterocyclic compounds may be found in Lange's Handbook of Chemistry (Ref. 10).

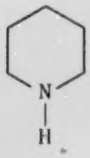


Figure A-6. Piperidine.

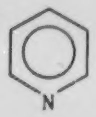
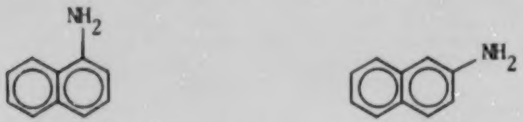


Figure A-7. Pyridine.

McKee and Wolf (Ref. 6) list toxicity data for several amines. Aquatic toxicity (48-hr TL_m) with the creek chub is ca. 85 mg/l for diethylamine, ca. 40 mg/l for ethylamine. Methyl amine is more toxic: $LC_{100} \approx 30$ me/l. Aniline is less toxic for several species (0.2 to 1.0 g/l). Pyridine had a 96-hour TL_m of 1.3 g/l with mosquito fish. Other aquatic toxicity data for these and many other amines are also presented.

Non-aquatic toxicity data are listed in Table III of Reference 5 for other amines which are potential water pollutants. Particular attention should be given to the aromatic amines which have been shown to be carcinogenic (Table V, Ref. 5). Among these, α- and β-naphthylamine (Fig. A-8) and benzidine (Fig. A-9) are petrochemicals used in the dye industry which have been recently cited as extremely hazardous (Refs. 11, 12). Non-aquatic toxicity data on other petrochemical amines can be found in Reference 7. For example, ethyleneimine (Fig. A-10) is about 100 times more toxic to laboratory animals than ethylamine. Both are completely soluble in water.



α- or 1-　β- or 2-

Figure A-8. Naphthylamines.

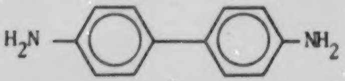


Figure A-9. Benzidine.

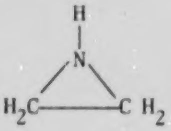


Figure A-10. Ethyleneimine.

Amine petrochemicals are not only toxic water pollutants at mg/l to g/l concentrations, but they also are vile smelling and tasting at concentrations below the acutely toxic level. For example, pyridine is reported to impart a characteristically unpleasant odor to water at 2.5 mg/l. Fortunately, most petrochemical amines can be biodegraded rather rapidly with the proper seed organisms (Ref. 6).

6.2 Nitrogenous Heterocyclic Hydrocarbons

Cyclic hydrocarbons which contain N in the ring structure are known as nitrogen heterocycles. This category overlaps with some of the amines discussed above, *viz.*, pyridine, piperidine and ethyleneimine. However the N-heterocycles also encompass non-basic compounds which are not considered strictly amines. The nitrogens in these hydrocarbons may be neutral or even acidic. An example of a mildly acidic N-heterocycle is indole (Fig. A-11). Chemically, indole has a greater tendency to release a hydrogen ion (H^+) as an acid than to accept one as a base. At 5 mg/l indole is reported to cause distress or death to trout but not to sunfish or sea lamprey (Ref. 6). It is a highly odoriferous compound which may lead to tainting of fish flesh or water supplies.

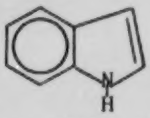


Figure A-11. Indole.

6.3 Nitriles

Alkyl and aryl cyanides (nitriles) are a category of petrochemicals containing C, H and N whose chemical behavior is unrelated to the foregoing C, H and N categories. Nitriles are characterized by possession of an organic cyano group ($-C{\equiv}N$). This functional group when bonded to an alkyl or aryl functional group constitutes a nitrile.

Despite the presence of a cyano group, nitriles do not ordinarily release cyanide ion ($C{\equiv}N^-$) upon decomposition in the aquatic environment or in living systems. The covalently bonded cyano group is not particularly reactive chemically. Under rigorous conditions in the laboratory the cyano group can be hydrolyzed to the amide, displaced by anions or reduced to the amine. On the other hand, presence of the cyano group can serve to activate adjacent double bonds to undergo various types of reactions useful industrially.

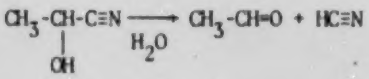
Acrylonitrile (Fig. A-12) is perhaps the most important nitrile petrochemical. McKee and Wolf (Ref. 6) describe it as a "flammable liquid used in the manufacture of plastics and synthetic rubber, and as a pesticide fumigant for stored grain." Since it is used as a fumigant, it is not surprising

$$H_2C{=}CH{-}C{\equiv}N$$

Figure A-12. Acrylonitrile.

that acrylonitrile is one of the most toxic nitriles. It is also moderately soluble in water. McKee and Wolf (Ref. 6) list extensive aquatic toxicity data on acrylonitrile which indicate that it is hazardous to many fish at 20 mg/l and above. Microbial growth is also affected at these levels with fungus inhibited least. Compared to acrylonitrile, benzonitrile (phenyl cyanide) is only about half as toxic to fish and acetonitrile (methyl cyanide), a widely used solvent, is only ca. 1% as toxic.

Reference 5 tabulates much of the same data presented earlier in Reference 6. Data are also given for lactonitrile (Fig. A-13); however technically it is not an alkyl cyanide but a cyanohydrin, a relatively unstable adduct of hydrogen cyanide (HCN) and acetaldehyde. Facile reversibility of this reaction in water or tissue yields (HCN) which accounts no doubt for its high toxicity: 24 hr $TL_m < 1$ mg/l for many species.



$$CH_3\text{-}\underset{\substack{|\\ OH}}{CH}\text{-}C{\equiv}N \xrightarrow[H_2O]{} CH_3\text{-}CH{=}O + HC{\equiv}N$$

Figure A-13. Decomposition of lactonitrile in water.

7. Oxygenated Hydrocarbons

The oxygenated hydrocarbons are a large class of petrochemicals containing oxygen (O) as well as C and H. Oxygen can be incorporated in a variety of ways which gives rise to numerous functional groups. Presence of O in the molecule renders it more water soluble than the parent hydrocarbon molecule. Oxygenated petrochemicals containing one or two carbons (C_1 - C_2) are highly soluble in water. Thereafter water solubility falls off with increasing ratio of C to O, depending on the characteristics of the particular functional group. According to the practical rule that "like dissolves in like," compounds with hydroxy functional groups (acids, alcohols, enols, phenols) are more soluble than those with ether and carbonyl functional groups (ethers, esters, aldehydes, ketones). Compounds with one oxygen functional group are not likely to be miscible with water above the C_3 level. As would be expected, additional oxygen functional groups promote increased water solubility.

Oxygenated hydrocarbons are discussed briefly below according to functional groups. Each functional group category itself could be dealt with as an entire section, as phenols have been (see "Phenols", H2O-PHE); however, this discussion must be confined to selected highlights.

7.1 Alcohols

Alcohols are hydroxylated hydrocarbons produced in large quantities, generally from alkenes (olefins). The simplest alcohol, methanol (CH_3-OH), is an exception, being produced from methane (natural gas). Alcohols are used extensively both as industrial solvents and as chemical intermediates.

Alcohols in the aquatic environment may be more of a nuisance than a toxic hazard. Most are readily metabolized microbially which contributes to the BOD burden of petrochemical effluent. Unlike methyl and ethyl alcohols, many of the alcohols above C_2 impart an unpleasant taste to water which must be eliminated in public water supplies.

McKee and Wolf (Ref. 6) discuss the aquatic toxicity of allyl, amyl, benzyl, butyl, ethyl, methyl, octyl, and propyl alcohols. Allyl alcohol appears to be the most toxic to aquatic life followed by n-octyl alcohol. They describe allyl alcohol as "lethal" to bivalve larvae at 2.5 mg/l and "harmful" to rudd at 10 mg/l. n-Octyl alcohol paralyzed goldfish in 15 minutes at 67 mg/l. The "critical ranges" for other alcohols with the creek chub, a fish with average tolerance, are listed in Table A-3. All four test fish survived for 24 hours below this range; all four died above it.

Table A-3.

Critical Range of Alcohols for the Creek Chub

(from Ref. 6)

Alcohol	Critical Range in mg/l
n-propyl alcohol	350-500
n-amyl alcohol	350-500
mixed primary isoamyl alcohols	400-600
isopropyl alcohol	900-1100
n-butyl alcohol	1000-1400
tertiary amyl alcohol	1300-2000
tertiary butyl alcohol	3000-6000
ethyl alcohol	7000-9000
methyl alcohol	8000-17000

7.2 Aldehydes

Aldehydes are intermediate in oxidation state between alcohols and carboxylic acids. They are characterized by the presence of a $-C^{\nearrow O}_{\searrow H}$

group. Generally, aldehydes are chemically reactive, tending to oxidize or polymerize readily. They also tend to be more noxious and toxic than their alcohol analogs.

An aqueous solution of formaldehyde (HCHO) called formalin is familiar as the eye-smarting preservative used for biological specimens. McKee and Wolf (Ref. 6) list extensive aquatic toxicity data for formaldehyde. Ca. 30 mg/l is critical for rainbow trout and chinook salmon. For fingerling channel catfish the 24-hr TL_m is 32 mg/l, the 48- and 96-hr TL_m is 25 mg/l. The catfish can survive 18 mg/l for three days; trout, 10 mg/l. Threshold effects were noted in *Daphnia* at 2 mg/l during 2 days, in *Scenedesmus* at 0.3 mg/l during 4 days.

Acetaldehyde (CH_3-CHO) is less toxic. The 96-hr TL_m for sunfish is 53 mg/l. The 24-hr TL_m for marine pin perch is 70 mg/l; no deaths occurred at 60 mg/l. Both aldehydes inhibit oxygen utilization in microbial cultures above 150-200 mg/l although accommodation may occur.

Acrolein (H_2C=CH-CHO) is a highly toxic aldehyde sometimes employed as an aquatic pesticide. Chinook salmon are very sensitive to acrolein: 24-hr TL_m = 0.08 mg/l. Otherwise, 1-5 mg/l is critical for many species of fish and other aquatic life.

7.3 Carboxylic Acids

Acrylic, maleic, phthalic, and terephthalic acids are typically produced as petrochemicals for use in polymers. Aquatic toxicity data are sparse on these and other petrochemical carboxylic acids.

7.4 Esters

Esters are less water soluble than most oxygenated hydrocarbons. McKee and Wolf (Ref. 6) list aquatic toxicity data for typical esters. For example the 24-, 48- and 96-hr TL_m for isoamyl acetate with mosquito fish is 65 mg/l. The critical range for creek chub is 50-120 mg/l. Threshold of harmful effects were noted at 120 mg/l for *Daphnia* (2 days) and at 180 mg/l for *Scenedesmus* (4 days). For these latter two species the values for n-butyl acetate are 44 mg/l and 320 mg/l, respectively.

Diethyl phthalate, a solvent for varnishes, killed a goldfish in 30 min at 1.2 mg/l (Ref. 6). Neither Ref. 4 nor 5 lists aquatic toxicity data for other phthalate or terephthalate diesters although they are commonly associated with plastics, particularly dibutyl phthalate. Concern is growing over the increasing evidence of dibutyl phthalate in the aquatic environment.

7.5 Ketones

Ketones are the least water soluble of the oxygenated hydrocarbons. They are widely employed as solvents and as important chemical intermediates in the synthesis of organic chemicals. Ketones appear to be less toxic to aquatic life than most oxygenated hydrocarbons. Acetone (dimethyl ketone: CH_3COCH_3) is completely soluble in water. It is very widely used in many commercial processes, being derived along with phenol from the oxidation of cumene. Lethal concentrations of acetone for most species are $\geq$ 10 g/l. Threshold effects approach 1 g/l (Ref. 6). Methyl ethyl ketone (MEK: $CH_3COCH_2CH_3$) is almost as innocuous. Sunfish and mosquito fish gave 24- and 48-hr TL_m values of 5.6 g/l for MEK (Ref. 6). Sunfish however were visibly affected at 3.4 g/l. No aquatic toxicity data were available for cyclohexanone, derived from phenol and used to make Nylon-6 (Ref. 5, 6).

7.6 Ethers

Most petrochemical ethers appear to be relatively harmless to aquatic life. Ethylene oxide ($H_2C\overset{O}{\text{—}}CH_2$), produced in quantity from ethylene, may be an exception. It is used to make ethylene glycol and its polymers, and acrylonitrile. Ethylene oxide is also used as a fumigant for foodstuffs and textiles, a sterilant for surgical instruments, and an agricultural fungicide (Ref. 7). These biocidal properties, combined with its complete solubility in water, suggest that ethylene oxide is a petrochemical which should be carefully monitored in industrial discharges related to its use. No aquatic toxicity data are listed in References 5 or 6. The fact that it is a gas at ambient temperatures and pressures suggests its potential hazard to both the aquatic and air environments.

Two related cyclic ethers, propylene oxide ($H_2C\overset{O}{-}CH\text{-}CH_3$) and epichlorohydrin ($H_2C\overset{O}{-}CH\text{-}CH_2Cl$) would be expected to pose similar problems although neither is as water-soluble or volatile. Another extremely toxic ether, bis-chloromethyl ether, fortunately decomposes in water to the less lethal hydrochloric acid (HCL) and formaldehyde (HCHO) (Ref. 6).

8. Miscellaneous Organics

Within the loose definition of petrochemicals (page 1, H2O-PET) there are a number of compounds, including by-products, which do not fall into the broad categories of sections 4 through 7. Quantitatively they are minor, however, selected examples merit brief mention.

8.1 N and O Containing Organics

Petrochemicals containing both N and O are confined mainly to nitroaromatics ($ArNO_2$), oximes, amides, and isocyanates. Nitration of benzenoid compounds is the primary route to the aromatic amines which are important to the Dye industry. Limited aquatic toxicity data are available for nitroaromatics (Ref. 6). Nitrobenzene is moderately soluble in water. Marine fish show irritation at 10 mg/l; ca. 20 mg/l is lethal to minnows in distilled water but not in hard water. The threshold of toxicity is 30-40 mg/l for *Daphnia*, *Microregma* and *Scenedesmus*. Cyclohexanone oxime and caprolactam (Figure A-14) are petrochemical intermediates in the synthesis of Nylon-6 from methane. No aquatic toxicity data was available (Ref. 5-8).

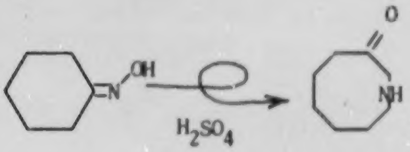


Figure A-14. Conversion of cyclohexanone oxime to caprolactam.

Isocyanates are monomers for polyurethanes. They are composed of one or more isocyano functional groups (-N=C=O) bonded to an alkyl or aryl group. Although highly toxic in the vapor state (Ref. 7, 8), isocyanates decompose rapidly in water to the corresponding primary amine.

8.2 Sulfonate Detergents

Sulfonates are important petrochemical products widely employed as detergents. They are salts of organic sulfonic acids with the general formula of $R\text{-}SO_3H$, where R is an organic radical, either alkyl or aryl. Early detergents were the highly branched alkyl benzene sulfonates (ABS). However, they proved too resistant to biodegradation in sewage treatment plants. It was found that when a "straight chain" alkyl group was substituted for the highly branched alkyl group, biodegradability became much more acceptable. As a result most sulfonate detergent sold today is the linear alkyl sulfonate (LAS). LAS came into use in the mid-1960's after publication of Reference 6. Reference 5 contains no LAS toxicity data. Both sources list extensive concentration and BOD data on ABS. Just prior to printing this section, Water Quality Criteria 1972 (ref. 12) became available. Discussion and data pertinent to detergents in Ref. 12 appears as an Appendix to Section A.

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APPENDIX

Water Quality Criteria 1972

A Report of the
Committee on Water Quality Criteria

Environmental Studies Board

National Academy of Sciences
National Academy of Engineering

Washington, D.C., 1972

FOAMING AGENTS

"FOAMING AGENTS" (from Section II - Public Water Supplies p. 67)

Many chemical substances occurring either naturally or as components of industrial or domestic waste will cause water to foam when agitated or when air is entrained. The most common foaming agent in use today is the synthetic anionic surfactant, linear alkyl benzene sulfonate (LAS). Branched alkyl benzene sulfonate (ABS) was used prior to 1965 as a base for synthetic detergents. Because of its persistent foaming properties, however, ABS was replaced by LAS. The most objectionable property of surfactants is their foaming capacity which can produce unsightly masses of foam in a stream or at the home tap. The surfactants also tend to disperse normally insoluble or sorbed substances, thus interfering with their removal by coagulation, sedimentation, and filtration.

Although conversion to the more readily biodegradable linear alkyl sulfonates by the detergent industry has decreased the persistence of sulfonates in aerobic waters, measurable concentrations of these substances still can be found in both surface and ground waters. Concentrations of anionic surfactants in water can be determined by means of their reaction with methylene blue dye (Standard Methods 1971).[162] Concentrations of less than 0.5 mg/l, as methylene blue active substances (MBAS), do not cause foaming or present serious interference in the defined treatment process and are well below the inferred limit (700 mg/l) of toxicity to humans based on tests on rats fed diets of LAS (Buehler et al. 1971).[161] It must be recognized that this procedure does not determine the total concentration of foaming agents, merely the concentration of materials that react with methylene blue, most of which are anionic surfactants. Although cationic and nonionic synthetic surfactants do not respond, and not all substances that respond to the methylene blue process cause foaming, the methylene blue test is the best available measure of foaming properties.

Recommendation

To avoid undesirable aesthetic effects and because the defined treatment process does little or nothing to reduce the level of foaming agents, it is recommended that foaming agents determined as methylene blue active substances not exceed 0.5 mg/l in public water supply sources.

FOAMING AGENTS

[161] Buehler, E. V., E. A. Newmann, and W. R. King (1971), Two-year feeding and reproduction study in rats with linear alkylbenzene sulfonate (LAS). *Toxicol. Appl. Pharmacol.* 18:83–91.

[162] Standard methods (1971) American Public Health Association, American Water Works Association, and Water Pollution Control Federation (1971); Standard methods for the examination of water and waste water, 13th ed. (American Public Health Association, Washington, D. C.), 874 p.

"DETERGENTS" (from Section III - Freshwater Aquatic Life & Wildlife p. 190-191)

Detergents

Detergents are a common component of sewage and industrial effluents derived in largest amounts from household cleaning agents. In 1965 a shift from tetrapropylene-derived alkylbenzene sulfonates (ABS) to the more biodegradable linear alkylate sulfonates (LAS) was made by the detergent industry. In current detergent formulas, LAS is the primary toxic active compound, two to four times more toxic than ABS (Pickering 1966).[534] However, toxicity of LAS disappears along with the methylene blue active substances (MBAS) response upon biodegradation (Swisher 1967).[537] Retrieval of MBAS data from the National Surveillance Stations throughout the U.S. from 1966 to the present showed that the mean of 3,608 samples was less than 0.1 mg/l. There has been a downward trend in MBAS concentrations. Only four stations reported mean concentrations greater than 0.2 mg/l.

The MBAS determination has been the routine analytical method for measurement of surfactant concentrations. Positive errors are more common than negative ones in the determination of anionic surfactants in water (Standard Methods 1971).[536] An infrared determination or a carbon absorption cleanup procedure is recommended when high MBAS concentrations are found.

Marchetti (1965)[533] critically reviewed the effects of detergents on aquatic life. Most available information on LAS toxicity relates to fish. Short term studies by a number of investigators have shown that lethal concentrations to selected fish species vary from 0.2 to 10.0 mg/l (Hokanson and Smith 1971).[532] Bardach et al. (1965)[531] reported that 10 mg/l is lethal to bullheads (*Ictalurus* sp.), and that 0.5 mg/l eroded 50 per cent of their taste buds within 24 days. Thatcher and Santner (1966)[538] found 96-hour LC50 values from 3.3 to 6.4 mg/l for five species of fish.

Pickering and Thatcher (1970)[535] found in their study of chronic toxicity that a concentration of 0.63 mg/l had no measurable effect on the life cycle of the fathead minnow (*Pimephales promelas*), while a concentration of 1.2 mg/l was lethal to the newly hatched fry. A safe level should be between 14 and 28 per cent of the 96-hour LC50. Hokanson and Smith (1971)[532] reported that a concentration of 1 mg/l was an approximate safe concentration for bluegills in Mississippi River water of good quality. Arthur (1970)[530] found that the no-effect level of LAS on *Gammarus pseudolimnaeus* was 0.2 to 0.4 mg/l. This investigator also subjected opculate and pulmonate snails to 60-week exposures of LAS and showed the toxicity levels to be 0.4 to 1.0 mg/l and greater than 4.4 mg/l, respectively.

Recommendation

Once a 96-hour LC50 has been determined using the receiving water in question and the most sensitive important species in the locality as the test organism, a concentration of LAS safe to aquatic life in that water can be estimated by multiplying the 96-hour LC50 by an application factor of 0.05; but no concentration greater than 0.2 mg/l is recommended at any time or place.

DETERGENTS

[530] Arthur, J. W. (1970), Chronic effects of linear alkylate sulfonate detergent on *Cammarus pseudolimnaeus*, *Campeloma dicisum*, and *Physa integra*. *Water Res.* 4(3):251–257.

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[536] Standard methods (1971) American Public Health Association, American Water Works Association, and Water Pollution Control Federation (1971), Standard methods for the examination of water and waste water, 13th ed. (American Public Health Association, Washington, D. C.), 874 p.

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B. ANALYSIS

Monitoring petrochemical pollutants in water is important for two reasons:

a) Most petrochemicals are biodegradable organic compounds which represent a source of biochemical oxygen demand (BOD). Hence, large scale release of petrochemical wastes to receiving waters without adequate pretreatment can deplete the dissolved oxygen (DO) with accompanying serious consequences. BOD analysis is discussed under "Biological Parameters" (H2O-BIO).

b) Petrochemical effluent may exert acute or chronic toxic effects on aquatic life in the receiving waters. If such receiving waters are also sources of drinking water supplies, they need to be monitored for petrochemical contamination both before and after purification treatment.

1. Sampling

Sampling of petrochemicals generally follows the same principles discussed under Section B-1 of Pesticides (H2O-PES). If discrete grab samples are to be taken, it is important that the containers be inert, nonabsorptive and free from organic contaminants such as plasticizers. In general, this requires previously cleaned glass bottles equipped with screw cap lids and Teflon liners for effective sealing (Ref. 1).

Petrochemical samples should be analyzed as soon as possible after collection. This minimizes sample loss through biodegradation and, with the highly volatile petrochemicals, evaporation. Refrigeration may be advisable if analysis must be delayed for a few hours. Flash freezing with liquid nitrogen may be required if the sample can not be analyzed the same day.

2. Sample Preparation

Preparation of water samples for analysis for petrochemical content varies according to the physico-chemical properties of the petrochemical(s) in question. Highly volatile, slightly water-soluble petrochemicals such as ethylene, propylene, and butadiene may require entrainment in a stream of purge gas (nitrogen, argon or helium) followed by trapping in a suitable absorbent (e.g., molecular sieve).

Less volatile, slightly water-soluble petrochemicals may require extraction by a volatile water-immiscible solvent (hexane, ether, chloroform, etc.) prior to analysis. This is useful in concentrating the petrochemicals in the aqueous sample, however the solvent and extraction conditions must be chosen to be compatible with the petrochemicals to be analyzed and the analytical method. For example, if the analysis is to be performed on gas chromatography (GC) the solvent must not obscure any of the sample components. The solvent also must be compatible with the analytical technique. For example, chlorinated solvents should be avoided if electron capture (EC) GC is used. On the other hand, flame ionization detection (FID) GC is compatible with direct injection of aqueous samples.

A number of petrochemicals are >10% soluble in water (see Table A-1). If these organics are sufficiently concentrated (e.g., >1 mg/1) direct analysis by FID-GC may be preferable to extraction. If extraction is desired, such compounds may have to be rendered less soluble by increasing the ionic strength of the aqueous sample through addition of salts. Some of these water-soluble petrochemicals such as ethylene glycol or glycerol (glycerine) may require formation of a chemical derivative prior to GC analysis to assure suitable chemical stability and volatility. With hydroxyl functional groups, conversion to a silyl ether derivative is a common procedure. Carboxylic acids may be converted to their corresponding methyl esters to improve GC characteristics.

3. Gas Chromatography (GC)

Almost all petrochemicals can be analyzed qualitatively and quantitatively by gas chromatography. Some aspects of GC analysis are discussed in several of the other sections of this volume. See "Pesticides" (H2O-PES), Section B-7; "Phenols" (H2O-PHE), Section B-3, 6, 7; and "Oil and Grease" (H2O-OIL), Section B-1. Abundant GC analytical data is available on petrochemicals, although it may be widely dispersed in the scientific literature. GC manufacturers brochures contain example gas chromatograms for many of the important petrochemicals. The even-year "Analytical Reviews" in Analytical Chemistry (Ref. 2) are a valuable source of GC information for many substances, including most petrochemicals. The most comprehensive storehouse of GC data is to be found in Gas Chromatography Abstracts (Ref. 3).

Briefly, gas chromatography is a method whereby highly to moderately volatile compounds are transported in a carrier gas through a tube containing a stationary interactive medium which delays transit of the sample compounds according to their physicochemical properties. Various methods are available to detect the emerging organic compounds from the tubing of "column" and measure the amount present.

3.1 Thermal Conductivity Detection (TCD)

The thermal conductivity detector is a cell which compares the thermal conductivity of two gas streams: (a) the GC column effluent stream of carrier gas and separated sample components and (b) a reference carrier gas stream equal to (a) but containing no GC sample. These two gas streams pass over separate heated resistors (filaments or thermistors) which are resistance arms of a balanced Wheatstone bridge circuit. In absence of sample components, the sample sensing stream, (a), and the reference stream, (b) are adjusted to cool their respective heated resistors equally and the bridge remains in electrical balance. The carrier gas, usually helium, is chosen for its very low heat capacity compared to other substances. This means that when a separated sample component emerges from the GC column in stream (a), it will cool the sensing resistor more than the reference carrier gas stream cools the reference resistor. When this happens the cooler sensing resistor displays an increased resistance which can be measured from the bridge circuit on a millivolt strip-chart recorder.

The TCD is very close to being a universal detector for gas chromatographable substances. This includes gases such as ethylene and propylene. It is especially popular for analyzing gas mixtures containing components which cannot be detected by the FID. The main disadvantage of the TCD is that it is among the least sensitive of the GC detectors. Also it becomes less efficient as the operating temperature increases. For these reasons it is employed mainly to analyze gaseous mixtures at or near room temperature.

3.2 Flame Ionization Detection (FID)

Details of the flame ionization detector are given under "Oil and Grease" (H2O-OIL) in Section B-1.1. The FID comes very close to being a universal detector for gas chromatographable *organic* substances. It has good sensitivity (< 1 ng) and can be used for all organic petrochemicals. It has the added advantage over the TCD that it does not respond to water and most other inorganic gases and vapors. This allows direct GC analysis of water samples for petrochemicals where desired. Figure B-1 shows the analysis of a typical petrochemical plant effluent by FID-GC. Each "peak" represents one or more organic compounds.

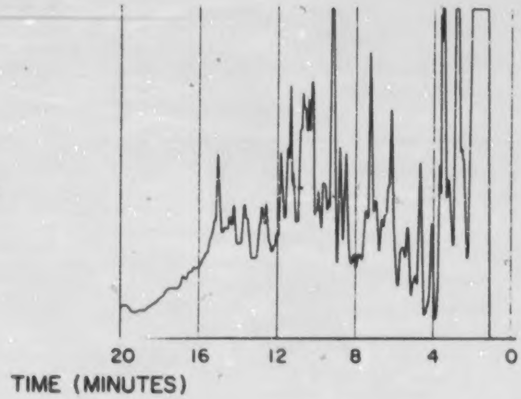

Figure B-1. Gas chromatogram of petrochemical plant effluent (from Ref. 4).

3.3 Specialized Detectors

Detectors which respond more selectively to a limited number of chemical types are discussed under (a) "Pesticides" (H2O-PES), Section B-7.2, and (b) "Oil and Grease" (H2O-OIL), Section B-1. The electron capture detector (ECD; H2O-PES, Section B-7.2.1) is highly sensitive (< 1 pg) to halogenated organics, nitro organics and polyaromatics. The alkali flame ionization detector (AFID) or thermionic detector (TID) can be used for sensitive (< 1 ng) detection of nitrogen containing organics [see "Pesticides" (H2O-PES) Section B-7.2.4]. Other detectors suitable for analysis of nitrogen, sulfur or phosphorus containing organics are also discussed under "Pesticides" (H2O-PES), Sections B-7.2.2, -7.2.3, and -7.2.5.

4. Confirmatory Techniques

When all the petrochemicals (organics) in a water sample are compounds already known to be present, it is generally not too difficult to determine which GC peak in the gas chromatogram corresponds to which petrochemical contaminant in the water sample. This is usually accomplished by chromatographing a known reference sample of a petrochemical under identical GC conditions employed with the environmental sample. When the retention time of a reference compound matches the retention time of a GC peak in the environmental sample, a tentative identification has been made. If more than one reference compound has the same retention time under these GC conditions, the identification remains ambiguous.

Rechromatography under conditions which separate these references is necessary to clarify the tentative identification. It is also customary to check for exact retention time match by chromatographing a mixture of the environmental sample enriched with some of the reference compound. This should be done separately for each reference standard.

Although the above procedure may establish the identity of an organic to a high degree of probability, the identification remains tentative until confirmed by independent analysis by at least one other technique. Rechromatography on a substantially different GC column may be helpful, however the best confirmation of identity involves collection of the separated GC sample component so that it can be subjected to a definitive spectroscopic analysis. This includes infrared (IR), ultraviolet (UV), nuclear magnetic resonance (NMR), and organic mass spectroscopy (MS).

When the absolute quantity of a petrochemical contaminant in an environmental sample is too low to permit efficient GC collection (e.g., <0.2 mg) and subsequent spectroscopic analysis, it may be possible to feed the GC effluent (carrier gas + entrained sample component) to a highly sensitive, rapid-scanning spectrometer for analysis "on-the-fly". So far, only MS and IR are capable of this arrangement. Combined GC-MS is in use throughout the EPA regional laboratories, whereas combined GC-IR remains largely under study.

5. Combined Gas Chromatography-Mass Spectrometry (GC-MS)

Combined gas chromatography-mass spectrometry is extremely important for analysis of trace levels (< 0.2 mg) of unknown petrochemicals and by-products in complex mixtures. The gas chromatograph provides good to excellent separation of multicomponent mixtures. Mass spectrometers designed to receive the GC effluent for instant mass spectroscopic analysis are capable of producing a mass spectrum of the GC effluent every 1 to 3 sec. Sensitivity of detection and identification depends on the mass spectrum of each compound. Generally, identification is feasible at the nanogram level if the gas chromatograph has performed a clean separation from most other GC sample components.

An extensive description of combined GC-MS is presented in Section B-9 under "Pesticides" (H2O-PES). The reader is referred there for further details. The Methods Development and Quality Assurance Research Laboratory of the EPA in Cincinnati, OH, has published a useful and informative newsletter (Ref. 5) on the use of GC-MS to identify organic pollutants in water. This publication has been reproduced as Appendix I to this section to which the reader is referred.

6. REFERENCES

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3. Gas Chromatography Abstracts, Preston Technical Abstracts Co., P.O. Box 312, Niles, IL 60648.

4. M. D. Lair, R. G. Rogers and M. K. Weldon, "Environmental Effects of Petrochemical Waste Discharges on Tallaboa and Guayanilla Bays, Puerto Rico," Technical Study TS 03-71-208-02, EPA Region IV, Athens, GA (October, 1971).

5. J. W. Eichelberger, L. E. Harris and W. L. Budde, "Identifying Organic Pollutants in Water," News of Environmental Research in Cincinnati, March 22, 1974, EPA, Cincinnati, OH 45268 (Appendix, this section).

7. PETROCHEMICALS INSTRUMENT NOTES

The instruments used for monitoring petrochemicals in water have been largely covered in other sections. Almost all petrochemicals (or suitable derivatives) can be analyzed by gas chromatographs either directly or in solvent extracts. Detergents are the exception. They are analyzed colorimetrically. Colorimeters appear under Metals (H20-MET, Section B.3; UV-Visible).

Gas chromatographs appear elsewhere in this volume in four main categories:

a. single or dual GC column, isothermal oven, flame ionization detection (FID): Instrument Notes under "Phenols" (H20-PHE, section B. 12).

b. dual GC column, temperature-programmable oven, dual FID: Instrument Notes under "Oil and Grease" (H20-OIL, section B. 8).

c. single column, isothermal oven, single electron capture detection (ECD): Instrument Notes under "Pesticides" (H20-PES, section B. 12: GC-ECD).

d. single or dual column, isothermal or temperature programmable oven, element selective detector (FPD, MCD, CCD, TID): Instrument Notes under "Pesticides" (H20-PES, section B. 12: GC-FPD, GC-MCD, GC-CCD, GC-TID).

The above Instrument Notes also list alternative options and models under "Features," "Remarks," and "Multi-Parameter Capability."

Gas chromatographs/mass spectrometer/data systems will be listed also under "Pesticides" (H20-PES, section B. 12).

APPENDIX I.

News of Environmental Research in Cincinnati
U.S. Environmental Protection Agency

METHODS DEVELOPMENT
AND QUALITY
ASSURANCE
RESEARCH

March 22,
1974

IDENTIFYING ORGANIC POLLUTANTS IN WATER

J. W. Eichelberger, L. E. Harris, and W. L. Budde*

BACKGROUND

Identifying and measuring specific organic compounds that contaminate the environment has concerned environmental research scientists for many years. The huge number of potentially harmful or toxic compounds that are theoretically possible has discouraged the development of a specific analytical method for each. Instead, general approaches based on slight differences in solubility, chromatographic behavior, and spectroscopic measurements were developed and used widely to gain information about the types of compounds present in various samples.

Unfortunately, many of these standard techniques of chemistry, which provided very valuable information in flagrant pollution situations, were either slow, expensive of skilled manpower, or relatively insensitive to very small quantities. In addition, most of these techniques frequently failed to generate really definitive information. As a result, environmental researchers began to turn to a new multidisciplinary technique: computerized (automated data processing) gas chromatography/mass spectrometry (ADP/GC/MS).

This sophisticated technique was developed during the 1960's primarily to meet the demand of basic research workers in medical, biochemical, flavor, odor, medicinal, and geochemical research. Basic research supported by the National Institutes of Health, the National Science Foundation, and the National Aeronautics and Space Administration played the major role in the development of the concept. Since one of the basic problems of each of the above areas of research is the identification and measurement of trace quantities of a great variety of organic compounds, the application of the technique to environmental research was obvious but slow to come about.

Like any automated method, ADP/GC/MS does not reduce the need for skilled manpower; in fact, it requires highly skilled, multidisciplinary teams of spectroscopists, analytical chemists, electronics engineers, and laboratory minicomputer specialists. The major advantage of this method is that it enormously increases the capacity of a fixed or limited staff to make large numbers of unambiguous identifications of specific organic compounds in environmental samples. Identification of noxious pollutants at the part-per-billion level with a high degree of confidence in the result has become nearly routine in more than a few U.S. Environmental Protection Agency (EPA) laboratories. What once was a nearly impossible task for a staff of 100 working for 6 months sometimes can be accomplished by several people in a few hours.

STATE OF THE ART

EPA has made a major commitment to ADP/GC/MS during the last few years by installing about 23 complete systems valued at about $2.5 million in laboratories across the country. The systems are employed in eight regional surveillance and analysis laboratories, both National Field Investigations Centers, two National Environmental Research Center (NERC) – Cincinnati laboratories, one NERC-RTP laboratory, six NERC-Corvallis laboratories, and two Office of Pesticide Programs laboratories. The annual total costs dedicated to these systems should be at least equivalent to the purchase price.

System Operation

Eighteen of the systems mentioned above are nearly identical Finnigan quadrupole mass spectrometers computerized with Digital Equipment Corporation PDP-8 minicomputers* (Figure 1). The three functional parts of the systems are as follows:

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*Mention of commercial products does not imply endorsement by the EPA.

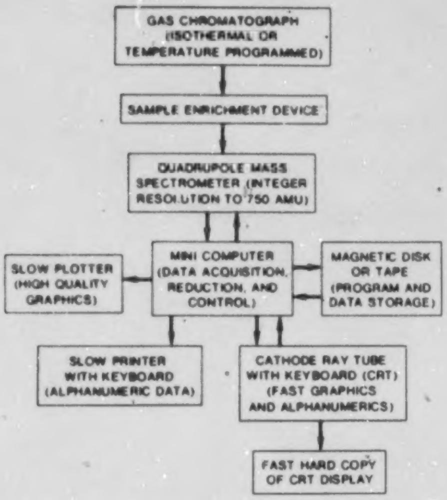
GAS CHROMATOGRAPH (ISOTHERMAL OR TEMPERATURE PROGRAMMED)
SAMPLE ENRICHMENT DEVICE
QUADRUPOLE MASS SPECTROMETER (INTEGER RESOLUTION TO 750 AMU)
SLOW PLOTTER (HIGH QUALITY GRAPHICS)
MINI COMPUTER (DATA ACQUISITION, REDUCTION, AND CONTROL)
MAGNETIC DISK OR TAPE (PROGRAM AND DATA STORAGE)
SLOW PRINTER WITH KEYBOARD (ALPHANUMERIC DATA)
CATHODE RAY TUBE WITH KEYBOARD (CRT) (FAST GRAPHICS AND ALPHANUMERICS)
FAST HARD COPY OF CRT DISPLAY

Figure 1. Configuration of the ADP/GC/MS system widely used in EPA.

(1) The gas chromatograph is very well established as a powerful tool for the separation of complex mixtures of volatile organic compounds. However, since conventional GC detectors provide too little information about the sample, they have been removed.

(2) The MS is the only GC detector used, and like conventional GC detectors, it is very sensitive. In contrast to the single-channel response of conventional GC detectors, the MS provides a multichannel response that carries a great deal of information about the molecular structure and composition of organic compounds. This information may be displayed graphically by a fast cathode-ray tube or a slow (pen + ink) plotter, printed in digital form, or transmitted over conventional voice-grade telephone circuits to other data-handling systems.

(3) The minicomputer makes the hookup possible. In noncomputerized systems, mass spectra generally are not acquired continuously during the GC run. Continuous mass spectra acquisition generates very significant information that cannot, however, be processed economically or accurately by hand. This dilemma is solved in a computerized system. Mass spectra are acquired continuously, and the minicomputer handles all this information and controls the operation of the MS simultaneously. The MS data are acquired and processed by the computer and stored temporarily on a magnetic disk or magnetic tape before plotting, printing, or transmission. Personnel who previously devoted long, unproductive hours to manual data processing are freed to do productive tasks such as data interpretation.

Methods Development and Quality Control

The Methods Development and Quality Assurance Research Laboratory (MDQARL) of NERC-Cincinnati is involved in a number of projects in ADP/GC/MS, including the development of detailed methods for use of this equipment. Of course, the manufacturers of the equipment provide basic operating instructions for the systems. But, since they manufacture equipment for use in a wide variety of applications (from cancer research to identification of drugs in racehorse urine), they cannot possibly provide detailed methods for any one of them. Methodology is needed for analytical quality control, preanalysis sample preparation, more efficient separations, special MS techniques, and data interpretation. Since ADP/GC/MS is a computerized tool, some of the methodology needed can be incorporated into minicomputer programs that can be used by well-trained operators.

Quality control techniques are of special interest, of course, to encourage the production of the valid mass spectra that are required to make correct identifications. A properly operating, well-tuned ADP/GC/MS is required to obtain a valid mass spectrum. MDQARL has developed and distributed a procedure that uses a standard reference compound to make a quick check (about 15 minutes) of the performance and proper tuning of a system. With a minimum expenditure of time, an operator using this procedure can be reasonably sure that the GC column, the sample enrichment device, all components of the MS, the data acquisition system, the data reduction system, and the data output system are all functioning properly. After an unsuccessful test, the individual subsystems must be examined and the faulty component corrected. Data acquired after a successful system check are validated and far more valuable than unvalidated data. Data acquired after an unsuccessful test may be worthless and cause erroneous identifications.

The reference compound yields fragments in its mass spectrum that are distributed fairly evenly up to mass 450. This feature allows the operator to check the low-, medium-, and high-mass range sensitivity and resolution. During the checkout procedure, the operator obtains a gas chromatogram and a mass spectrum of the reference compound. The peak in the chromatogram is observed for sharpness, size, and shape. This is a check on the GC column, sample enrichment device, and overall spectrometer sensitivity. The mass spectrum is compared with a list of quality criteria obtained from an interlaboratory study and repetitive analyses. Favorable comparison indicates proper performance of the system. A supply of the reference compound is maintained for distribution as requested.

Other MDQARL Projects

Some other current projects at MDQARL include an evaluation of direct aqueous injection analyses, the use of support-coated open tubular GC columns, investigations of new packed GC columns, research on techniques for the quantitative measurement of the pollutants detected, and the development of computer programs for data interpretation.

These techniques are intended for laboratories that will use ADP/GC/MS to:

- identify organic compounds in industrial effluents for background data or enforcement action;
- characterize oil spills;
- determine organic compounds as the cause of taste and odor in drinking water supplies;

- evaluate the effectiveness of treatment systems designed to remove organic pollutants;
- study the accumulation of organic pollutants in aquatic life; and
- determine the causes of fish kills.

Direct Aqueous Injection. Direct aqueous injection analysis is the introduction of a few microliters of water sample into the ADP/GC/MS instead of an organic solvent extract. The direct analysis of water samples with GC is not a new technique, but its employment with a MS as a GC detector is new. This procedure enables the analyst to identify volatile components that are normally lost during extract concentration or components that do not extract because they are too water soluble.

The minimum detectable concentration using direct aqueous injection is 1 to 5 ppm, depending on the compound observed. Although the method is not very sensitive, it is suitable for analysis of many industrial wastes. The following compounds have been detected in some industrial waste samples using direct aqueous injection: methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, acetone, acetic acid, propanoic acid, butanoic acid, N,N-dimethyl formamide, 2-ethoxyethanol, 2-butoxyethanol, and methylene chloride.

Extraction with an Organic Solvent. Many types of compounds have been detected in industrial waste samples by extracting them with an organic solvent, such as methylene chloride, concentrating them into a very small volume, and injecting a small portion into the ADP/GC/MS. The sensitivity is greatly increased with the extraction procedure, and as little as 0.1 ppb of a compound can be detected in a liter of water. The following list, though by no means complete, does name some of the most interesting compounds detected in industrial wastes by solvent extraction: N-methylcarbazole, t-butylanisole, benzonitrile, trichlorophenol, fluorene, pyrene, indole, naphthol, alpha terpineol, o-phenylphenol, pentachlorophenol, and methylnapthalene.

Interpretation of Data

The necessary prerequisite of effective data interpretation in ADP/GC/MS is the availability of valid mass spectra. Assuming that the ADP/GC/MS is well tuned and in good operating condition, the only other requirement for valid mass spectra is the clean separation of the individual components of a mixture on the GC column. This is, of course, the classical problem of chromatography, but it is made somewhat more manageable with the MS detector. An experienced user can frequently ascertain that the separation is clean and free of overlaps by an examination of the internal consistency of the MS data. This is not possible with the simpler, conventional GC detector.

There are two fundamentally different approaches to the identification of specific organic compound pollutants from valid mass spectra. Interpretations may be attempted based on the theory of mass spectra and the rules of fragmentation of organic ions in the gas phase. Unfortunately, this approach is frequently slow and tedious and requires Ph.D-level training or experience. However, it is generally far more definitive than the equivalent approach with other types of spectrometry (e.g., infrared spectra). This approach is clearly justified when all else fails in important situations such as an enforcement action or fish kill.

The alternative is the purely empirical method of searching a file of reference mass spectra to find a similar or exact match of the experimental spectrum. Manual searching of printed data is rather slow, subject to human error, and intellectually unstimulating. Computerized searches overcome these problems, and two experimental remote systems are in use by EPA. The two systems are markedly different in their approach to the problem and both are described briefly. Perhaps the simplest approach would be to utilize the PDP-8 minicomputer and disk or tape available on the MS data system to search a data base of reference spectra. This may be the most economical method, but it has not been developed fully and is not currently used by EPA.

One system used by EPA was developed by the Battelle Memorial Institute with funding from the Southeast Environmental Research Laboratory component of NERC-Corvallis. It is intended to be used by a laboratory technician who needs to know the correct buttons to operate and the correct commands to enter. MS data are transmitted in batches directly from the ADP/GC/MS data system to a large Control Data Corporation model 6400 computer at Battelle-Columbus via standard voice-grade telephone lines. The system is highly automated, rather sophisticated, and makes good use of the data. It is simple to use because it either finds a match or it doesn't, and if it doesn't, there are no other alternative modes of search. The system does require the ADP/GC/MS data system, and ADP/GC/MS is precluded during its use.

The other system used by EPA was developed by the National Institutes of Health (NIH) and may be used by any EPA laboratory under an existing EPA-NIH interagency agreement. This system runs on a large Digital Equipment Corporation model PDP-10 computer at the NIH computer center in Bethesda, Maryland. The user enters MS data via a standard keyboard/printer terminal connected to a standard voice-grade telephone line and does not utilize the resources of the ADP/GC/MS data system. The matching system is highly interactive and conversational, and the user must impose his judgment in entering data. This system is oriented to the experienced user who sits in the interactive loop with the computer program and has many optional approaches to probing the data base and searching for a match. This approach makes less efficient use of computer resources and depends more on an operator's judgment to make good use of available data. However, it is a more flexible method, especially when an exact match is not available. For economy and additional flexibility, these two experimental systems will probably be combined with the same data base on the same time sharing computer in the near future.

EPA-MS USERS GROUP

In the spring of 1972, MDQARL organized an EPA-MS users group. The purpose of the group is to promote the informal exchange of technical information among the EPA laboratories using the 23 computerized GC/MS systems. The group is designed to be especially helpful to laboratory personnel (e.g., regional surveillance and analysis chemists) who are just beginning to acquire the skills necessary to utilize this sophisticated equipment effectively. In addition, the group keeps all involved personnel up-to-date on the latest instrumental improvements, new techniques, new equipment additions, and new software programs and capabilities.

CONCLUSION

It has been clearly demonstrated that ADP/GC/MS can provide extremely high quality and highly significant information about organic environmental pollutants to environmental scientists and enforcement officials. However, the achievement of this capability requires a substantial laboratory management commitment.

The ADP/GC/MS is not the kind of equipment that can stand idle for weeks and then be used effectively by occasional users. Users require in-depth knowledge, and the equipment requires routine maintenance, adjustment, and utilization. Furthermore, the commercial packages are not perfected and will require updating in the future. Nevertheless, we deeply believe that the commitment is worth it and that ADP/GC/MS routine analyses should replace, in many EPA laboratories, some of the traditional water pollution methodology that generates less relevant and very much less significant data.

WATER POLLUTION CONTROL TECHNOLOGY ASSESSMENT

An Environmental Resources Conference, May 1-3, Columbus, Ohio

The sessions, cosponsored by the U.S. Environmental Protection Agency and Battelle's Columbus Laboratories, will be held in the Battelle auditorium. Additional information may be obtained from either G. R. Smithson, Jr. (program) or D. A. Yothers (arrangements) at Battelle's Columbus Laboratories, 505 King Avenue, Columbus, Ohio 43201; telephone (614) 299-3151. Registration fee for the conference is $60.

UNITED STATES
ENVIRONMENTAL PROTECTION AGENCY
NATIONAL ENVIRONMENTAL RESEARCH CENTER
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Oil and Grease
OIL

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FOR

OIL AND GREASE IN WATER

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A. INTRODUCTION

The grounding of the supertanker *Torrey Canyon* (Ref. 1, 2) off the coast of England with the release of 30 million gallons of crude oil on March 18, 1967 set in motion a chain of events which constitutes a watershed in man's awareness of the hazards of aquatic oil pollution and his concern for its prevention and control (Ref. 3). On May 28, 1967 President Johnson directed the Departments of Interior and Transportation to examine how the resources of the nation could best be mobilized against oil-spill pollution. As a result, *Oil Pollution -- A Report to the President* was issued in February 1968 (Ref. 4). Oil spilled on water was characterized as "one of the most devastating substances in the environment." Of even greater concern, the country was found "not fully prepared to deal effectively with spills of oil or other hazardous materials - large or small - and much less with a *Torrey Canyon* type disaster."

Since issuance of the above report, some progress has been made in the detection of oil spills (Ref. 5-7), the identification of the source of the spill (Ref. 8-13), and the cleanup of oil spilled (Ref. 14-26). More progress will be required, particularly in prevention and cleanup, before our aquatic environment can be assured of minimal adverse effects from oil pollution (Ref. 2, 27-31).

The problems created by the *Torrey Canyon* and other large disasters are fairly obvious and more readily studied than the immense number of daily small discharges of oil to the aquatic environment. So long as the developed nations of the world, particularly the U.S., depend upon petroleum to fuel and lubricate their technologically oriented societies, the problem of controlling aquatic oil pollution will exist. The objective of this survey is to describe analytical instrumental procedures suitable for detecting and characterizing aquatic oil pollution sufficiently well to trace the pollution to its source for remedial action and impact study.

Most of the attention to the problems of oil in water since *Torrey Canyon*, concerns oil pollution on the open seas and coastal areas (owing to heavy maritime petroleum traffic and increased offshore exploration and production). The scope of this survey of water quality instrumentation is not directly involved with marine applications; however, since much of the technical discussion in the technical and mass media on marine oil pollution also applies to oil pollution of inland waterways (e.g., estuaries, lakes, canals, rivers, etc.) material concerning marine oil pollution is also included.

A number of commendable references are available. An excellent, general discourse on oil pollution appeared in the second edition of *Water Quality Criteria* (1963, California, Ref. 32). More recently a number of conferences on oil pollution have been held in this country. The published proceedings are listed as Ref. 14-16, 33. Other informative general references include publications of the Federal government (Ref. 4, 29, 34, 35) and bibliographies (Ref. 36-41).

1. Historical Aspects

Petroleum (rock oil) has been known to man for at least six millenia. Earliest known usage was in the vicinity of the oil seeps in the Black and Caspian seas (Ref. 42, 43), where oil was employed for some of the same uses it is put to now, viz., cooking, heating, lubrication, road-building, etc. These seepages were regarded as obnoxious by the local populace (Ref. 43), suggesting that the concept of aquatic oil pollution is not new. Natural seepages are found throughout the world (Ref. 44, 45) and are believed to constitute an environmental insult (Ref. 28). When compared to the volume of oil contamination resulting from current technological exploitation of petroleum, the estimated quantity of oil introduced into the aquatic environment as a result of natural seepages is relatively minor (Ref. 30).

Early recorded comment on inland oil pollution characterized the Caspian Sea in 1754 as greatly spoiled due to leakage of oil carried in wooden-hulled ships (Ref. 46). Similar problems existed with oil barges on the Volga until stone ballast was added to increase the draft and hence the hydrostatic pressure outside the hull. Contamination of water resources by oily matter, primarily petroleum and its products, is a natural consequence of the exponential growth of the petroleum industry. For example, in 1860, one year after the first successful domestic producing well was established, world petroleum production ran around 0.5 million barrels. A century later it had grown to 7 billion barrels. It has more than doubled in the decade since (Ref. 43).

One of the early major domestic oil-spill incidents involved the tanker *Santa Rita* in San Francisco Bay in 1907 (Ref. 47). A sizeable spillage of fuel oil cargo was ignited by sparks from a dock locomotive, and the resulting fire endangered nearby shipping. The steady climb in oil pollution levels in the decades to follow appeared not to crystallize public concern until the tanker sinkings along the coast during World War II resulted in beach pollution too serious to ignore (Ref. 43).

In recent times, a number of serious inland incidents have occurred (Ref. 4). Compared to the major marine oil spillages, e.g., Torrey Canyon (30 million gallons), Ocean Eagle (1 million gallons) or Platform A in the Santa Barbara Channel (200,000 gallons), inland spills in general are smaller. However, this may not always be the case. A recent barge tow on the Mississippi and Ohio rivers amounted to about one-third of the Torrey Canyon load (i.e., 10 million gallons) and exceeded it in length (Ref. 24).

2. Characteristics

As applied to water quality considerations, the pollutant "oil" can cover a number of types of materials: Petroleum (crude oil), petroleum products (gasoline, diesel fuel, lubricating oils, fuel oils, etc.) and, to a lesser degree, edible materials such as vegetable oils and animal fats. These diverse substances are distinguished by the following characteristics:

a) mostly organic chemical in composition
b) mixtures of molecules
c) mostly insoluble in water
d) generally lighter than water
e) liquid or fluid semisolid

Any type of material fulfilling all of these characteristics will certainly be characterized as oil pollution when encountered in the aquatic environment. However, without question, the problem of oil pollution is predominantly petroleum-oriented.

The physical behavior of oil in the aquatic environment is incompletely understood (Ref. 48-50). In general, surface crudes spread to very thin films and drift with the wind (2-4% of wind velocity) with a bias to the right of the wind in the northern hemisphere. According to the American Petroleum Institute (Ref. 51), at a concentration of 25 gallons/square mile, oil is barely visible; at twice that level (3.0×10^{-6} inch thickness) it appears as a silvery sheen. By doubling the concentration once again to 100 gallons/square mile, the first evidence of color appears. The wavelength of the color is indicative of the film thickness, and may be used to estimate the volume of oil present. After discharge on the sea, oil forms into large patches surrounded by a film of, presumably, the more mobile volatile components (Ref. 44). Sometimes evaporation, solution, or microbial degradation removes the film within hours, leaving slowly hardening pebble-sized lumps (tarballs) which resist further decomposition. The deleterious water in oil emulsion (dubbed "chocolate mousse" by the French) which washed ashore from the Torrey Canyon was tentatively attributed to the British use of detergent dispersing agents (Ref. 2) but now appears to be inherent with this and certain other crude oils (Ref. 64).

3. Sources

In 1970 the Federal government estimated that there were more than 7500 oil spills annually into the country's waters (Ref. 29), arising from such diverse sources as:

Vessels (spills, oily ballast/bilge discharge, sportcraft)
Pipelines
Rail and highway carriers
Land- and water-based storage tanks
Refining and other manufacturing operations
Jettisoning of fuel tanks by aircraft
On and offshore loading and unloading terminals
On and offshore drilling and production operations
Miscellany

Current estimates of annual oil spills run as much as 50% higher (Ref. 52).

Apart from the qualifying statistics, sources of aquatic oil pollution have been listed additionally as:

Civic and salvage dumps, garages, unburned fuel from ships' funnels (Ref. 32)
Gasoline service stations, municipal sewage systems (Ref. 4)
Unburned fuel from vehicles, locomotives (Ref. 30)

The citation of oil-spill occurrences along with quantitative estimates must be accompanied by the understanding that the data are not necessarily either precise or complete. The instances and amounts may well increase as techniques for reporting this information improve. Over a short period they may serve to illustrate the dimensions of the oil pollution problem. For example (Ref. 29):

Reported Oil Spills in U.S. Waters Over 100 Barrels (i.e., 4200 gallons)

	1968	1969
Vessels	347	532
Shore Facilities	295	331
Unidentified	72	144
TOTAL	714	1007

Oil spill data are not released to the public on a regular basis, however, the Environmental Protection Agency (EPA) reported the details concerning major oil spills within U.S. jurisdiction for the period of January 1, 1971 to June 30, 1971 in Table 1 (Ref. 54).

A discussion in depth of U.S. and world losses of oil to the aquatic environment is presented by Revelle et al. (Ref. 30).

Gasoline service stations annually dispose of 350 million gallons of used oil (Ref. 4, 29). It has been estimated that where waste lubricating oil is concerned, 37-40% is recycled, 12% is used on roads, 3% is used on farms, 23-25% is dumped on the ground, 1% is dumped directly into sewers, and 18-20% is unaccounted for (Ref. 53).

4. Effects

As stated by Clean Water for the 1970's (Ref. 29):

> Damages caused by oil pollution are both significant and diverse. Such pollution can destroy or limit marine life, ruin wildlife habitat, kill birds, limit or destroy the recreational value of beach areas, contaminate water supplies, and create fire hazards.

4.1 Effects on Man

The effects of aquatic oil pollution on man himself are quite minimal for the simple reason that he finds the prospect of oily water so aesthetically displeasing that he avoids personal contact with it. For further information see the National Technical Advisory Committee on Water Quality Criteria Report of 1968 (Ref. 35), under the Subcommittee for Recreation and Aesthetics. Contamination of domestic water supplies in particular must be avoided. The Subcommittee for Public Water Supplies (Ref. 35) made the following statement:

> It is very important that water for public water supply be free of oil and grease. The difficulty of obtaining representative samples of these materials from water makes it virtually impossible to express criteria in numerical units. Since even very small quantities of oil and grease may cause troublesome taste and odor problems, the Subcommittee desires that none of this material be present in public water supplies.

Aesthetic considerations predominate over toxicological considerations, as the following excerpt (references omitted) from McKee and Wolf (Ref. 32) serves to illustrate:

TABLE 1.

SOURCE	DATE	CAUSE	MATERIAL	VOLUME BBLS.*
Transmission Line	Jan 6	Rupture	Crude	4,048
Pipeline	Jan 8	Rupture	Crude	10,000
Navy barge	Jan 14	Sinking	Diesel	1,619
Oregon Standard	Jan 20	Collision	Bunker	20,000
Esso Gettysburg	Jan 23	Grounding	#2 Fuel Oil	8,600
Storage Tank	Jan 31	Tank Rupture	Crude	63,000
Idaho Standard	Feb 1	Grounding	Gas & Diesel	519
Barge	Feb 5	Grounding	Fuel Oil	976
Barge	Feb 16	Puncture	Gasoline	1,800
Storm Sewer	Feb 28	Unknown	Jet Fuel	3,571
Tug and Barge	Mar 1	Collision	Gasoline	1,786
Pipeline	Mar 5	Rupture	Crude	1,300
Pipeline	Mar 9	Unknown	Crude	3,700
Tank	Mar 23	Overflow	#6 Fuel Oil	1,428
Pipe	Mar 28	Leaking valve	Crude	500
Tank	Mar 30	Rupture	Gasoline	7,143
Pipe	Apr 5	Rupture	Bunker	1,650
Pipe	Apr 6	Rupture	Gasoline	1,429
Barge	Apr 26	Overflow	Diesel	5,550
Barge	May 11	Grounding	Kerosene	1,100
Tank	Jun 4	Puncture	JP4	1,071
Barge	Jun 12	Grounding	Crude	600
Dock	Jun 24	Unknown	Unknown	1,553
Pipe	Jun 25	Rupture	Crude	1,000

*1 BBL (barrel) = 42 U.S. gallons

> An exhaustive search of literature to determine the toxic components of refinery waste waters toward humans revealed a paucity of toxicological data on the ingestion of such substances by humans or by test animals. From the approximate order of magnitude based on data from the fields of occupational health and industrial hygiene, it was concluded that any tolerable health concentrations for oily substances far exceed the limits of taste and odor. It appears, therefore, that hazards to human health will not arise from drinking oil-polluted waters, for they will become esthetically objectionable at concentrations far below the chronic toxicity level.

Removing oil contaminants from domestic water supplies may be costly (Ref. 32):

> Floating or emulsified oil in raw-water supplies will complicate the coagulation, flocculation, and sedimentation processes at a treatment plant. Oil-coated floc may not settle properly. If free or emulsified oil reaches sand filters or ion-exchange beds it will coat the grains, decrease the effectiveness of filtration, and interfere with backwashing. Taste- and odor-producing compounds will require the greater use of activated carbon or heavy chlorination. Again, however, the taste-and-odor factor will control the threshold or limiting concentration of oily material acceptable in a domestic water supply.

4.2 Effects on Agriculture

The Subcommittee on Water Quality for Agricultural Uses (Ref. 35) made no specific recommendation in regard to contamination by oily substances. Some data are available on agricultural effects due to oil. Limited application of crude petroleum has been reported to improve rather than interfere with crops (Ref. 32). Farm animals have been reported to develop a fondness for crude oil and suffer adverse effects, including death, as a result (Ref. 55). An effluent standard of 30 ppm of oil emulsified in water was set by the Ohio Department of Health for a creek, due to its use by grazing cattle (Ref. 56).

4.3 Effects on Industry

The Subcommittee for Water Quality Requirements for Industrial Water Supplies noted (Ref. 35): "Steam generation and cooling are unique water uses in that they are required in almost every industry." Both functions are adversely affected by contamination with oil (Ref. 32): "In steam production, the presence of oil in boiler feed water may cause foaming, priming, overheating of tubes resulting in blistering or failure, and poor transmission of heat from the metal to the water." As a result, the American Boiler Manufacturers Association in its standard guarantee on steam purity specifies that "the total quantity of oil or grease, or substance which is extractable either by sulfuric ether or by chloroform, shall not exceed 7 ppm in the boiler water when the sample being tested is acidified to 1 percent hydrochloric acid, or 7 ppm in the feed water when the sample being tested is first concentrated at low temperature and pressure to the same ppm total solids as the boiler water." Additional examples of adverse industrial effects of oily water are reported in Reference 32.

4.4 Effects on Wildlife

Examples of wildlife flora and fauna which have benefited from the release of oily substances into their environment are few indeed. They appear to be limited to bacteria and fungi which feed on components of the oily matter, or to kelp which flourished apparently as a result of oil-implicated extermination of natural predators (Ref. 58). Otherwise, evidence is abundant that contamination of the aquatic environment with oily material is an adverse event, particularly for fauna. Numerous graphic examples are described in lay terms by Marx in his chapter "Oil vs. Marine Life" (Ref. 28). A more technical review is presented by Revelle et al. (Ref. 30).

McKee and Wolf (Ref. 32) summarize:

> Oil films may interfere with gas exchange, coat bodies of birds and fish, impart a taste to fish flesh, exert a direct toxic action on some organisms as a result of water-soluble components, and interfere with fish-food organisms and the natural food cycle. Oil from surface films becomes adsorbed on clay particles, settles to the bottom, and there remains a source of pollution, for it may be stirred up to float again or may leach toxic principles.

Most of the available toxicity data (see Ref. 32, 35) are reported as the median tolerance limit (TL_m), the concentration that kills 50 percent of the test organisms within a specified time span, usually in 96 hours or less. In many cases, the differences are great between TL_m concentrations and concentrations that are low enough to permit reproduction and growth. Aromatic hydrocarbons are generally implicated as the toxic components present in petroleum and its products.

Pickering and Henderson (Ref. 56) studied the toxicity of several important petrochemicals to fathead minnows, bluegills, goldfish, and guppies in both soft and hard water. Standard bioassay methods were used. The petrochemicals tested were benzene, chlorobenzene, o-chlorophenol, 3-chloropropene, o-cresol, cyclohexane, ethyl benzene, isoprene, methyl methacrylate, phenol, o-phthalic anhydride, styrene, toluene, vinyl acetate, and xylene. These were all similar in their toxicities to fish, with 96 hour TL_m values ranging from 12 to 368 mg/1. Except for isoprene and methyl methacrylate, which were less toxic, values for all four species of fish for the other petrochemicals ranged from 12 to 97 mg/1, a relatively small variation. In general, o-chlorophenol and o-cresol were the most toxic. Cairns (Ref. 57) reports the following 96 hour TL_m values of naphthenic acid for bluegill sunfish - 5.6 mg/1; pulmonate snail - 6.1 to 7.5 mg/1 (in soft water); and diatom - 41.8 to 43.4 mg/1 in soft water and 28.2 to 79.8 mg/1 in hard water. The term, naphthenic acid, refers to a family of cyclohexane carboxylic acids present in petroleum.

Surface oil films interfere with the respiration of aquatic insects (a fact used for control of the mosquito). Oil is also a well-known hazard to waterfowl (Ref. 4) by destroying the buoyancy and insulation of their feathers. The mortality rate of waterfowl which encounter oil slicks approaches 100%. The effects of marine oil contamination on flora and fauna have been even more striking. Several oil spills have been studied in extensive detail (Ref. 1, 16, 31, 58).

4.5 Criteria Recommendations

The criteria recommendations for water quality with respect to possible oil contamination have been listed in Reference 35 according to subcommittees for: Recreation and Aesthetics; Public Water Supplies; and Fish, Other Aquatic Life, and Wildlife. The summation of these recommendations constitute the overall recommendation of the first National Technical Advisory Committee on Water Quality Criteria (Ref. 35) with respect to oil in water. Criteria are intended to be scientific requirements on which a decision is to be made regarding what quality of water is suitable for a particular use. Water quality standards, established only by State (or Federal) authority, consist of accepted criteria plus implementation plans for pollution abatement measures necessary to meet the criteria (Ref. 29, 35). Federal/State water quality criteria on oil appear in Reference 59.

5. Control

So long as it is necessary to pump, transport and process petroleum or its products, the problem of aquatic pollution through accidental or careless spillage will continue. The best recourse to abatement is to institute procedures to reduce the opportunity for spillage and improve the cleanup. Far too much has been written on the various aspects of prevention, control and abatement of oil pollution to permit more than a brief coverage here. Some indication of the dimensions of the oil pollution problem can be seen in the report of the Secretary of the Interior, Clean Water for the 1970's (Ref. 29):

> Presently, the technology for coping with oil and hazardous materials spills is woefully inadequate. Prevention of accidents is the only sure way of protecting the environment. No completely effective techniques are available to control oil spills in the open ocean or lake waters. Wind and wave actions neutralize the effectiveness of oil spill containment devices, such as floating booms. Vacuum or scoop equipment to remove floating oils from the water does not accomplish the job, being effective only in rarely occurring calm seas. Chemical dispersants, sinking agents, and other materials are often ineffective and frequently very toxic to marine and wildlife. Common straw, which soaks up oil so that it can be removed, is still the standard material for fighting and cleaning up oil spills.

However, inadequacies in coping with oil in the aquatic environment do not result from a deficiency of approaches to the problem. Indeed, there are almost too many to choose from (see Ref. 14-26). Similarly, there is no lack of legal regulations governing, and in most cases prohibiting, the release of oily substances into receiving waters. As observed in the report to the President (Ref. 4), the essential elements of a program to cope with oil out of control are:

Prevention
Surveillance
Notification
Cleanup

Both legal and technological capabilities must be adequate.

5.1 Legal Aspects

The control of oil pollution is the subject of a number of laws. Tell (Ref. 60) has summarized the situation prior to the recent congressional session. The importance Congress attaches to the prevention and abatement of oil pollution is shown in the Federal Water Pollution Control Act of 1956 (33 U.S.C. 466 et seq.) as amended by the Water Quality Improvement Act of 1970 (Ref. 61). More space is devoted to oil pollution (Section 11) than to any other subject. The amended act specifically deals with the problem of oil discharges and provides for national effluent standards for oil (Ref. 60). Further amendments pertaining to oil pollution are contained in the Federal Water Pollution Control Act Amendments of 1972 (Ref. 62) and in the Ports and Waterways Safety Act of 1972 (Ref. 63).

5.2 Surveillance

The principle Federal surveillance activities for oil and other visible pollutants are conducted by the U.S. Coast Guard and U.S. Army Corps of Engineers. These agencies have responsibilities in the enforcement of statutes dealing with several phases of pollution control and have substantial numbers of persons engaged in water-related activities. The Environmental Protection Agency, through Technical Support Laboratories located within ten regions, supplies laboratory services necessary to establish the nature and source of oil spills. Cooperation with other federal and state agencies is an essential feature. At the direction of PL 91-224 the Council on Environmental Quality is responsible for preparing the National Oil and Hazardous Substances Pollution Contingency Plan (Ref. 34) to coordinate governmental response to oil spills.

5.3 Cleanup

Much has been written on cleanup procedures and techniques (Ref. 1, 2, 14-26, 28, 29). Pamphlets on particular methods (e.g., Ref. 17-26) are available from the Superintendent of Documents, U.S. Government Printing Office. The criticism of existing methods cited in section 5 (Ref. 29) is appropriate for most marine situations but perhaps overstates the case for a number of inland oil spill situations. Ludwigson (Ref. 2) has discussed the pros and cons of the various alternative methods dealing with oil spills, mentioning "booms of various types to contain oil slicks, skimmer boats to pick them up, pumps of various kinds, salvage considerations, collecting agents, sinking agents, gelling and congealing agents, and now even burning agents." Toxic hazards associated with detergent oil dispersants were also discussed.

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B. OIL SPILL IDENTIFICATION INSTRUMENTATION

In the previous section it has been shown that it is of utmost importance to detect, identify, and measure discharges of oil and grease into the aquatic environment to determine the nature of the offending material so that its source can be located and timely corrective measures instituted. This includes not only earliest possible termination of oil discharge, but also a thorough determination of the extent and amount of aquatic contamination to surface water, ground water, sediment, aquifer, fauna and flora to assess the environmental damage and the effectiveness of the cleanup. Oil processing and handling facilities would also benefit from the development of oil detection and identification techniques to pinpoint sources of spillage or leakage to surface or ground water or to determine the efficiency of oil recovery from processing water prior to release to receiving waters. With the assistance of modern analytical chemical technology, considerable progress toward this goal has been made.

Recently revised standard manuals on the analysis of water and waste water (Ref. 1-3) describe elementary methods for sampling, extracting (if necessary) and weighing oily or greasy (insoluble organic) material which may be present in water or waste water. Quantitation of such material is important in the treatment of sewage, because oily matter can interfere with bacterial degradation and plug carbon filters or render trickling ponds or sludge digesters ineffective. Quantitation is also essential to determine the levels of oil contamination dispersed throughout the aquatic environment.

Unfortunately, these elementary laboratory methods for measuring the bulk of insoluble organic matter in water and waste water offer little insight into the identity of the source of an unobserved oily discharge or its probable environmental impact. To determine these aspects, it is necessary to develop information on the composition of the oil, i.e., its constituent organic compounds. Because petroleum in particular is such a gross mixture of organic compounds, extensive detailed analysis of its composition has posed formidable difficulties in the past. In recent years a number of qualitative tests and analytical techniques have appeared in petroleum research and chemistry publications (see Ref. 4-6) which apply either directly or with modification to oil spill identification.

Because the various techniques employed in oil spill analysis are scattered throughout the technical literature, a standard manual setting forth analytical procedures in a generally accepted, systematized manner is a highly desired goal. As an initial response to this situation, a booklet entitled Laboratory Guide for the Identification of Petroleum Products (Ref. 7) was issued in 1969 by the Federal Water Pollution Control Administration (now the Water Quality Office, EPA). Besides describing additional sampling techniques, Reference 7 provides water pollution analysts with a series of specific analytical procedures. The purpose of these procedures is to characterize an unobserved oil spill sufficiently well to identify its probable source when compared with suspect samples. Offering suggested procedures on a trial basis exposes these procedures to the broad, general usage necessary for their acceptance as standardized methods. Although the booklet is incomplete by current standards and regional EPA laboratories already employ alternate approaches, it constitutes a useful initial step toward devising a systematic analysis of oily material in the aquatic environment. Parallel efforts by the American Society for Testing and Materials (ASTM), Subcommittee D-19.10 are underway (Ref. 8).

The choice of specific techniques from among the multiplicity of analytical procedures applicable to petroleum and its products depends on factors such as size, sampling methods, personal analytical preferences, and, perhaps most important, the availability of instrumentation. The more elementary bulk properties of an oil spill sample, such as density, viscosity, solubility in selected solvents, ash content, sulfur content, refractive index, distillation range, etc. can be used to characterize an unobserved oil spill for general classification purposes (Ref. 7). Gas chromatography (GC), atomic absorption spectrophotometry (AA), thin-layer chromatography (TLC), and infrared spectroscopy (IR) are examples of moderately sophisticated laboratory instruments which have been applied successfully to oil spill source identification by EPA technical support laboratories, among others. These latter instruments play an even more important role when assessment of the environmental impact of oil spills is the goal, since the questions of "what sort of" and "how much" noxious or toxic organic compounds are present require investigation into the molecular composition of the oily mass.

Because crude petroleum and many of its refined products represent an extremely complex and variable mixture of chemical compounds, mostly organic, no single analytical technique presently available is capable of analyzing this material *in toto*. However, the still-developing field of GC, in conjunction with ancillary techniques, most closely approaches this ideal; therefore, GC is the most important single technique. The sample requirements for a complex mixture like crude petroleum seldom exceed 10 milligrams for a dual detector GC run. Generally GC analysis is complemented with additional analytical data in order to establish conclusively the identity of an oil spill sample from among several similar suspected samples.

Atomic absorption spectrophotometry (AA), thin-layer chromatography (TLC) and infrared spectroscopy (IR) are currently the most utilized of the sensitive complementary techniques. All four techniques are limited in field applications to laboratory batch-type analysis as opposed to continuous, stream monitoring.

Although perhaps desirable, the present outlook for continuous, remote sensing, oil spill monitors out in the environment is not promising. This is due to a number of factors such as the tendency of oil to float on the surface where it is subject to wind drift, wave action, fluctuation with the water level, and adhesion to solid surfaces contacting it. Devices already suitable for refinery process monitoring (Ref. 9-11) become prohibitively expensive when adaptations for general remote environmental monitoring are considered. Airborne oil spill detection devices have been studied (Ref. 12-14). It must be kept in mind, however, that unless the oil slick detected is obviously linked, either through direct, unambiguous contact or strongly suspected recent contact, to the source of the discharge, detailed laboratory comparative analysis between the spill samples and suspect samples will be necessary to identify the source.

1. Gas Chromatography (GC)

The gas chromatograph is the most versatile and useful instrument for laboratory analysis of organic constituents in oil pollution samples. Available in the price range of $4,000 - $9,000 (including recorder), GC combines high detection sensitivity and extensive organic compound separation with comparative speed and ease of operation.

1.1 GC Operating Principle

As in other chromatographic methods, GC analysis consists of three essential steps:

(a) Sample introduction
(b) Sample movement through a selectively interacting immobile medium to separate sample components
(c) Detection of separated sample components at completion.

Basically gas chromatography consists of a partitioning effect on the sample components between existence as a vapor in the mobile phase (carrier gas) and existence as a solute in the stationary (liquid) phase.

As shown in Figure 1, the sample is introduced in liquid form by injection through a temperature-resistant silicon rubber diaphragm (septum) by means of a hypodermic type syringe especially miniaturized for GC. Upon injection the oil sample "plug" enters a chamber (heated inlet) with an elevated temperature adjusted to quickly vaporize the organic components. In the injection chamber the sample also encounters the flow of the inert mobile phase (carrier gas), usually helium (He), which transports the oil sample components through a tube (column) containing a thin film of immobile liquid (stationary phase) in intimate contact with the mobile vapor phase. Oil spill components (organic molecules) travel along the column according to their relative volatility and inversely according to their physicochemical affinity for the liquid stationary phase at the temperature of operation. The temperature and liquid phase are selected for their ability to separate the sample mixtures into their constituent compounds. After a characteristic interval (retention time), the individual separated components emerge from the column and are monitored by a sensing device (detector) that permits the recording of their passage as a time-based analog signal rising above the detector background signal (base line).

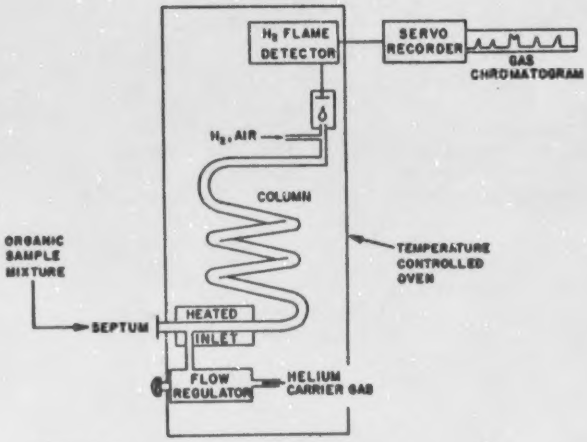


FIGURE 1. Gas Chromatograph.

A variety of permeable but low volatility polymeric liquids are available as stationary phases for oil analysis. To assure best operating performance and stability it is preferable to employ the highest temperature-rated liquid phases specifically prepared for GC use by vacuum stripping and catalyst removal (see commercial catalogs, Ref. 15-17). Also it is important that the liquid phase be present in a film thin enough to permit virtual instantaneous equilibration of the sample components between the liquid and vapor phase. At the same time it is necessary to have a sufficient quantity of liquid phase available so that it won't be swamped by the sample such that solute molecules act as solvent and "wash down" or strip the column. This requires a high surface to volume (or mass) ratio which has been achieved by supporting the liquid phase as a thin film on highly porous diatomite granules. The combination of stationary liquid phase on solid support is known simply as GC column packing.

Packed GC columns constitute the most widely utilized type; they exist in a variety of forms depending on how labile the sample components are and therefore how inert the GC column must be. This question is not so relevant to oil pollution analysis because most oil pollution constituents are stable to ordinary GC conditions. On the other hand, they compose such a complex mixture that the practical separating capability (or resolution) of packed columns (ca. 5000 effective plates [EP]) limits their utility. A second type, the small bore (0.010") open tubular (capillary) column has been employed with the film of liquid phase coated onto the inner wall of the tubing (stainless steel). Due to their comparative openness to flow, capillary columns can be extended to tens of meters in length without incurring prohibitive pressures as in the case of packed columns. Resolutions of the order of 50,000-200,000 EP are commonplace. The principal disadvantage of these columns is their low sample capacity which requires some means of attenuating the sample. Usually this is done with some sort of mechanical device called a splitter which divides the syringe injected samples pneumatically into two disparately-sized fractions. The larger portion is wasted by venting to atmosphere and the smaller portion becomes the sample analyzed by the capillary GC column. Approximate split ratios of 1/5 to 1/1000 generally are feasible and satisfactory, however splitters may be an unwelcome nuisance to the part-time GC practitioner.

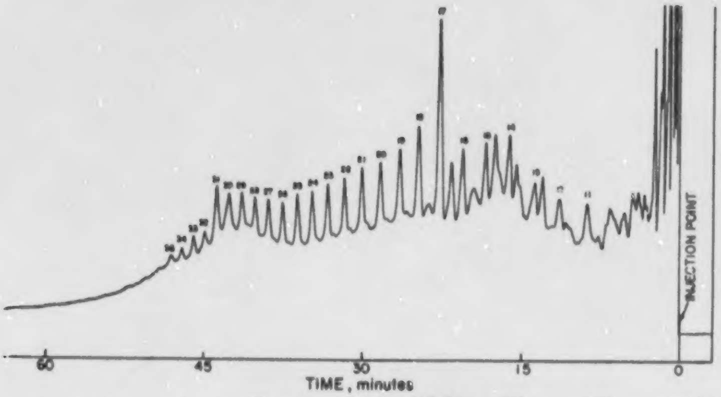
A third type of column available is a compromise between the packed and wall-coated columns, viz. the support-coated, open-tubular (SCOT) column. The SCOT column is similar to the wall-coated capillary in that the partitioning phase is coated along the wall which allows unimpeded flow. It also resembles the packed column in that fine particles included in the coating form a high-surface-area, porous support for the liquid phase. Thus samples may be injected (judiciously) without splitting and still undergo extensive separation (resolution: 20,000-40,000 EP).

Control of the operating temperature of the GC column oven is important to insure that the liquid phase is not overheated, and thereby decomposed or stripped. Most commercially available instruments not only provide for rapid, moderately accurate temperature control (±1°C) but also include the capability to increase the temperature at a selectable rate during the chromatographic run (chromatogram). This feature, known as temperature programming, is virtually imperative for separation and detection of complex mixtures of compounds found in oil spill samples. To achieve consistent, reproducible chromatograms, the septa must be leakfree and the carrier gas flow rate must be rigorously regulated, preferably within ±0.3%. For further discussion of pertinent operational factors see Reference 18.

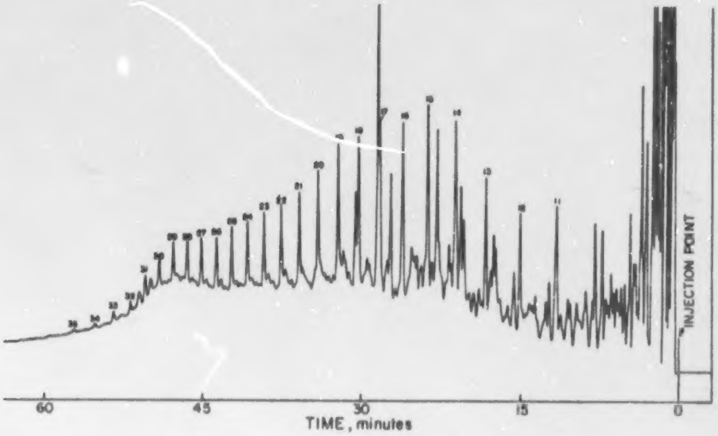
Once the oil spill sample has been separated into component organic compounds, a sensing device (detector) is needed to signal the emergence (elution) of the separated component from the column. Two similar devices which involve combustion are indispensable for the analysis of oily pollutants.

The first of these is the flame ionization detector (FID) in which the emerging (eluted) organic component is burned in a hydrogen-oxygen flame. Intermediate combustion states of the organic molecule exist briefly as ions which can be detected as a current between charged electrodes and amplified into a recorded signal. The FID has a wide range of linear sample concentration response with carbon sensing capability down to 10^{-12} g/sec. Except for highly oxidized carbon atoms within the organic molecule, the signal of this detector is directly proportional to the number of carbon atoms being burned, which provides a quantitatively comparable response for most compounds. Another advantage of this detector is that a number of substances such as nitrogen, carbon monoxide, carbon dioxide, water and carbon disulfide do not form ionized products in the hydrogen flame and hence do not interfere with the analysis of hydrocarbons.

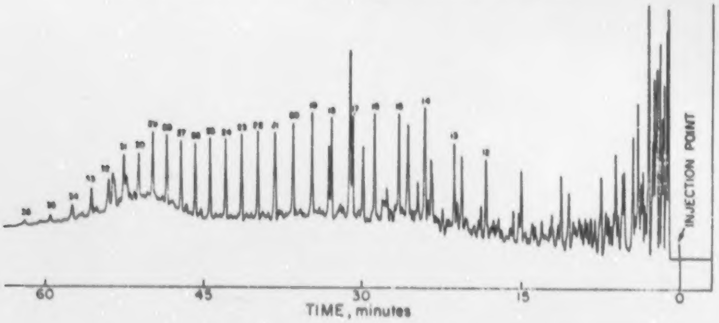
The second detector useful for oil pollution analysis operates on the principle of flame photometric detection (FPD). A flame similar to that used in the FID is employed except that it is richer in hydrogen. This feature causes sulfur present in the organic compound passing through the flame to emit light at the characteristic wavelength of 394 nm which is focussed, passed through a narrow band filter, and recorded on the output of a photomultiplier tube. Adlard (Ref. 20) has noted that the response of the FPD to organo-sulfur compounds is complicated by the presence of hydrocarbons in oil spill analysis, however it is not serious so long as a "unique and reproducible fingerprint for each crude oil" is produced. That this requirement is being met can be simply demonstrated by duplicate analysis in comparison with duplicate analyses of oil samples from a variety of other sources.



a. 1 m x 3 mm column packed with 3% OV-1 on Chromosorb G.



b. 50 m x 0.75 mm column coated with OV-101.



c. 20 m x 0.25 mm column coated with OV-101.

FIGURE 2. Nigerian crude oil. Flame ionization detector (FID) (from Ref. 20).

1.2 Oil Spill Identification by GC

Under appropriate conditions, GC is amenable to the extensive separation and detection of the constituent compounds in almost all petroleum products ranging from light oils to greases and tars. Options for varying the order of separating the components are also available, such as the choice of the partitioning agent (i.e., the stationary liquid phase), or the temperature program.

GC has the distinct advantage that more than one type of detector may be employed simultaneously during a single chromatogram. This provides a valuable second dimension of analytical data. For example, in crude petroleum analysis, constituent organic compounds may be detected, as they are separated from the sample mixture, on the basis of their sulfur content as well as their carbon content (FID vs. FPD) (Ref. 19, 20). Even though a single GC run may be incapable of separating all organic components into discretely detected individual compounds, the overlapped pattern (envelope) of detected compounds is still valuable as a distinguishing fingerprint characteristic of the particular sample. Dual detection (e.g., carbon/FID vs. sulfur/FPD) gives a dual profile of composition (fingerprint) which may be sufficient to identify the sample uniquely from among several suspected samples (Ref. 19, 20).

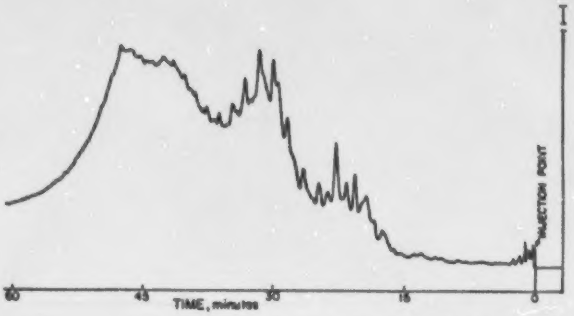
Other combinations of detectors sensitive to certain types of organic compounds could be employed in oil spill identification when the need and general relevance is demonstrated. These include:

(a) the electron capture detector (ECD) which is sensitive to organic halides (Cl, Br, I, and to a lesser degree F), conjugated carbonyls, polyaromatics, et al.

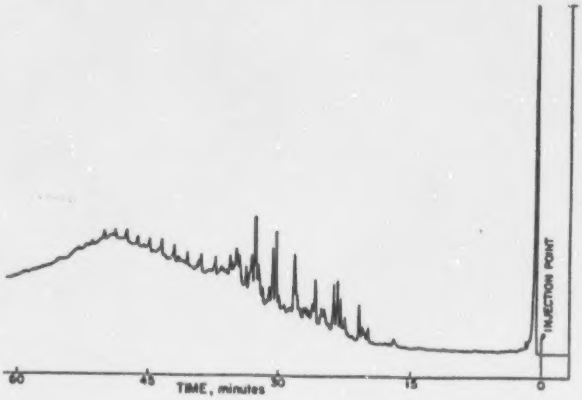
(b) the alkali-flame detector which is sensitive to organic phosphorous

(c) the microcoulometric detector which is primarily used for detecting Cl.

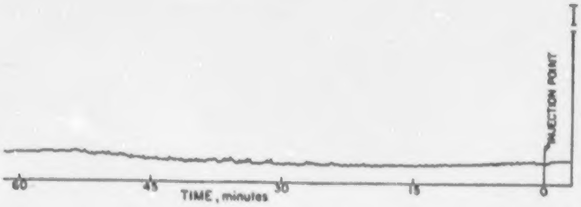
Figures 2 and 3 show gas chromatographic studies by Adlard et al. (Ref. 20) using three types of GC columns: (a) packed, 3mm I.D.; (b) capillary, 0.75 mm (0.030 in.) I.D.; and (c) capillary 0.25 mm (0.010 in.) I.D. Clearly the resolution of the chromatograms increases as the bore (I.D.) of the GC column decreases. In the case of the FID, an increasingly better defined profile of organic compound composition (based on carbon content) emerges (Fig. 2); however, in the case of the FPD the smallest bore capillary (Fig. 3c) cannot accomodate sufficient sample to give an adequate sulfur signal. Since SCOT columns (0.50 mm or 0.020 in I.D.) can accept samples comparable to the large-bore capillary (0.75 mm I.D.) (Ref. 21) with greater efficiency (i.e., comparable resolution in a shorter length), a 15-m SCOT column should afford a chromatogram (see Fig. 7) comparable to Figure 3b. For reasons mentioned here and above, SCOT columns offer, perhaps, an optimum compromise for oil spill analysis.



a. 1 m x 3 mm column packed with 3%w OV-1 on Chromosorb G.



b. 50 m x 0.75 mm column coated with OV-101.

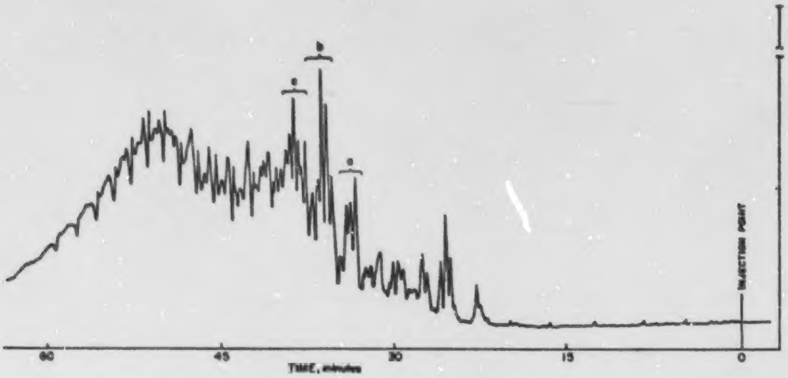


c. 20 m x 0.25 mm column coated with OV-101.

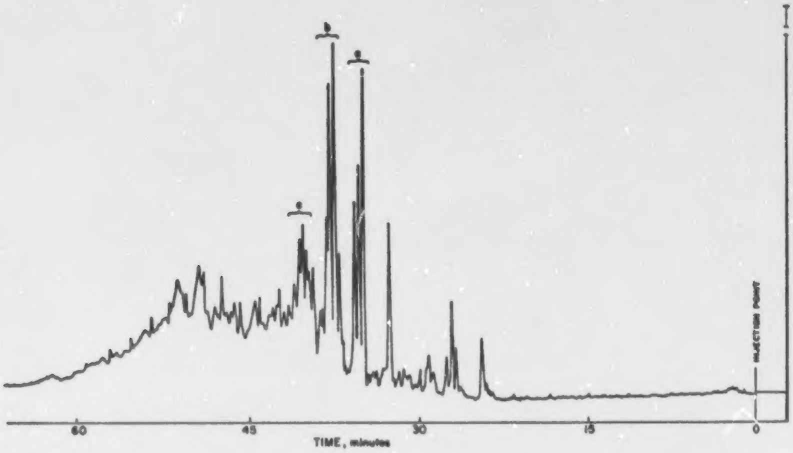
FIGURE 3. Nigerian crude oil. Flame photometric detector (FPD) (from Ref. 20).

Although the Nigerian crude oil in Figure 3c was too low in sulfur content to register on the FPD when chromatographed on the small capillary, Adlard et al. (Ref. 20) demonstrate that Kuwait and Qatar crudes can be analyzed for sulfur this way and easily distinguished from each other (Fig. 4). Even after biological degradation, the sulfur content profile of the Kuwait crude is readily recognizable by FPD (Figure 5a), whereas the FID chromatogram of the hydrocarbon composition (Figure 5b) is drastically altered in comparison with the unweathered version (Figure 6).

As can be seen by comparing Figures 2c and 6, the FID chromatograms of the Nigerian and Kuwait crudes are distinguishably different. Normal ambient weathering over a brief period



a. Kuwait crude oil.



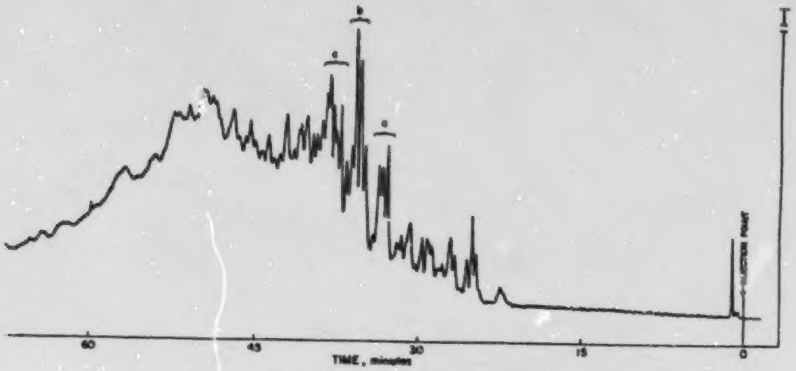
b. Qatar Marine crude oil.

FIGURE 4. Capillary chromatogram of unweathered crude oils. Flame photometric detector (FPD) (from Ref. 20).

of a few days would be expected to alter both of these chromatograms in the sense that the intensity of the GC peaks of the organic compounds would be expected to diminish progressively more moving from the 30 minute mark in the chromatogram to the origin. This corresponds to a general increase in volatility as the organic compounds become progressively lighter in molecular weight. Hence in samples weathered over a few days, it is not at all unexpected to observe a virtual absence of the "lighter ends" during the first 15 minutes of the FID chromatograms shown here, and sharply reduced peak heights during the second 15-min interval. Beyond this point any reduction in these relatively stable compounds would be attributable to biological degradation (see Fig. 5b) which favors consumption of the straight-chain (normal) saturated hydrocarbons (n-alkanes) over that of the branched and cyclic hydrocarbons.

The n-alkanes generally predominate over the others, as seen in the FID chromatograms (Fig. 2, 6) where the n-alkanes are listed according to carbon number. Loss of these numbered peaks due to bio-degradation would have a leveling effect on the entire chromatogram (Fig. 5b). On the other hand, usual ageing of agglomerated oil spill samples does not necessarily level the appearance of the n-alkanes (see Section A). Once these lumps (tarballs) form, bio-degradation becomes progressively less feasible, hence the n-alkane compositional profile (fingerprint) should remain intact inside the agglomerated portions. Analysis of the interior contents of tarballs should thus compare with the less volatile portion of the original material from C_{13} onward.

Overall, weathering/ageing/bio effects must be anticipated in GC analysis of oil spill samples, however the manifestations are quite



a. *Flame photometric detector (FPD).*

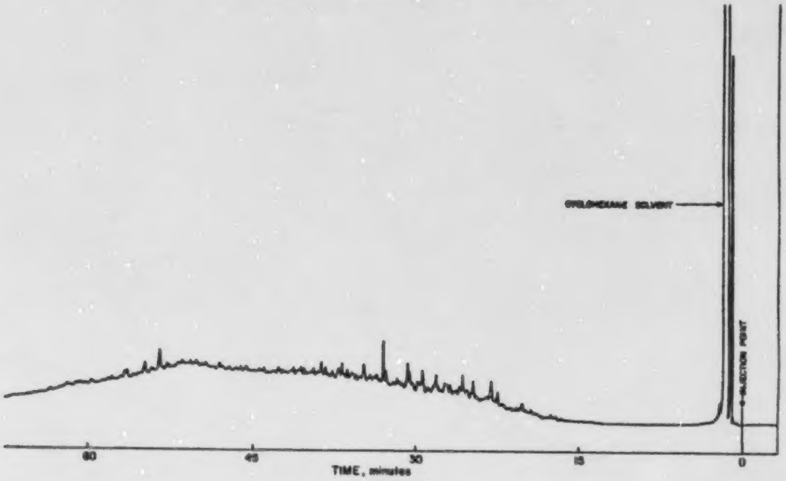


FIGURE 5. Capillary chromatogram of Kuwait crude oil biologically degraded (from Ref. 20).

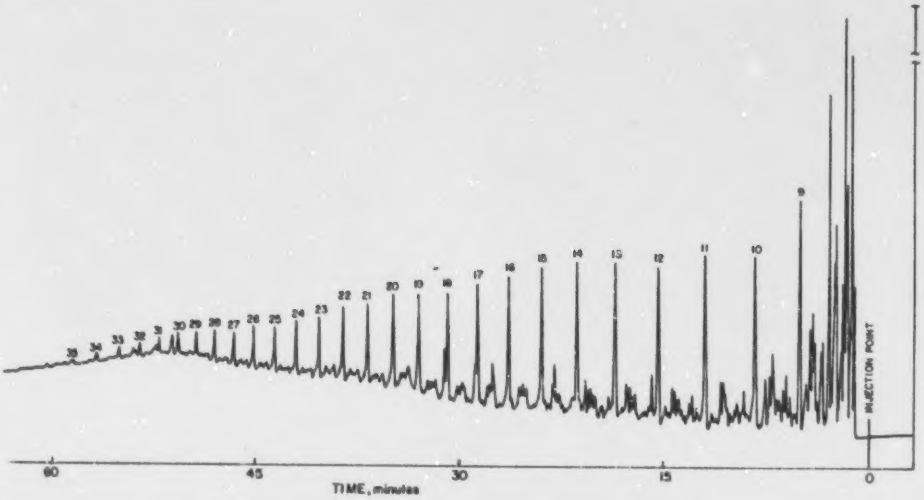


FIGURE 6. Capillary chromatogram of Kuwait crude oil, unweathered. Flame ionization detector (FID) (from Ref. 20).

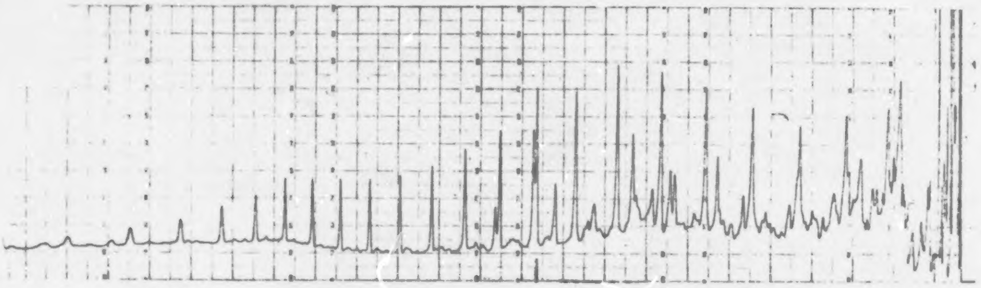


FIGURE 7. SCOT column chromatogram of Nigerian crude oil. Flame ionization detector (FID) (from Ref. 24).

rational in terms of the nature of the oily mass and do not defeat the utility of GC analysis for identification purposes.

Other GC methods for identification of oil pollution sources include a study undertaken in 1969 by the Western Oil and Gas Association (WOGA). Ten major oil company laboratories, four independent analytical laboratories, and one government laboratory participated. As reported by Kreider (Ref. 22), it was concluded that high resolution GC surpassed IR as the primary analytical technique. Importance was attached to having sufficient GC column resolution to separate the C_{19} isoprenoid (pristane) from n-C_{17} alkane and the C_{20} isoprenoid (phytane) from n-C_{18} alkane (see also Ref. 21 and 24 for discussions of these compounds). The WOGA subcommittee chose GC column parameters (Fig. 8) which represent a compromise between the first two choices (Fig. 2a, b) presented by Adlard et al. (Ref. 20). In essence, WOGA employed a packed column three times longer than specified in Figure 2a to increase resolution. Even so the resolution in Figure 8 is significantly less than attainable on capillaries (Ref. 19, 20; Fig. 2b, c , 6) or SCOT columns (Ref. 21, 24; Fig. 6).

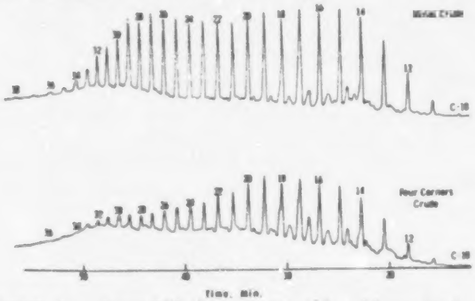


FIGURE 8. Paraffinic crude oils (from Ref. 22).

In an extensively detailed report to the EPA, Zafirou, Blumer and Myers (Ref. 24) describe successful application of SCOT GC columns to oil identification analysis. They place special emphasis on the capability to separate n-heptadecane (n-C_{17} alkane) from pristane and likewise, n-octadecane (n-C_{18} alkane) from phytane. They studied the relative abundancies of these four compounds and concluded that with appropriate manipulation these parameters could be used to correlate an oil spill sample with the correct suspect sample from among several candidates. As they correctly point out, bacterial degradation preferentially reduces the abundance of the n-alkanes (e.g., n-C_{17}, n-C_{18}) with respect to branched alkanes (e.g., pristane, phytane) which suggests that the use of normal/branched alkane abundancy ratios to correlate oil spill samples should be avoided except where the spill sample is too fresh to be degraded.

2. Atomic Absorption Spectrophotometry (AA)

A general discussion of the theoretical and practical aspects of AA analysis can be found in the section under Metals (H2O-MET). Essentially AA is a spectrophotometric method which takes advantage of the principle that an element in atomic form absorbs light at the same wavelength as that emitted by an excited atom of the same element. To analyze for a specific element, a light source from that element is employed. Sensitivities at or below the ppm level are generally attainable.

2.1 Oil Spill Identification by AA

Atomic absorption is useful for determining the levels of trace metals in crude petroleum and some of its products. Especially important are vanadium and nickel (Ref. 19, 25) which are relatively tightly bound (chelated) to organic compounds known as porphyrins. These trace metals in petroleum generally can be determined to 2-1/2 significant figures. Since they are not volatile under ambient conditions, they are not lost by evaporation when the oil spill mass is exposed to weathering processes. It is true that their concentration in the spilled oil will increase as the volatile portion is reduced by weathering; however, the ratio of the concentration of

V to Ni (V/Ni) will remain constant within experimental error. The concentration levels of V and Ni vary considerably throughout the world, and may even drift as petroleum is taken from the same well; therefore, the V/Ni ratio of concentrations is a batch characteristic which can be utilized as a marker to identify the samples from the same batch.

Stuart and Branch (Ref. 25) used V/Ni ratios to link pollution 100 miles offshore (Sable Island) with the wreckage of the tanker Arrow in Chedabucto Bay, Nova Scotia. The values reported (ppm) were:

	Chedabucto Bay	Sable Island
V	332	352
Ni	39	41
V/Ni	8.5	8.6

In this instance the effect of weathering to concentrate the trace metals is reflected in the higher offshore levels, however, the V/Ni ratio matches. In another case, pollution adjacent to a tanker was traced to its cargo of crude oil rather than a light residual fuel oil aboard a nearby naval vessel:

	Pollution Sample	Crude Oil	Residual Fuel Oil
V	54	44	49
Ni	5.3	4.1	10
V/Ni	10.2	10.7	4.9

As indicated above, both the individual concentrations of V and Ni as well as their ratio should be reported. In the second example the utility of using the V/Ni ratio to compensate for weathering again is evident. The V/Ni ratio was used to confirm GC identification of the tanker crude oil as the pollution source.

AA instrumentation is comparable in cost to GC, and is relatively simple to operate. The oil spill sample may not have to be ashed or dried prior to analysis, however it is necessary that the sample be in a homogeneous, nonviscous liquid condition (solution or stable emulsion). To accomplish this, any of a number of uncontaminated organic solvents (e.g., methyl isobutyl ketone, xylene) may be employed. AA spectroscopy is also useful in determining the metals present as soaps in greases (Li, Ba, Ca, Na, Zn, Pb, etc.) or lead (Pb) in gasoline.

3. Infrared Spectrophotometry (IR)

Infrared spectrophotometric analysis is used extensively to characterize organic compounds. Conventional organic infrared recording spectrophotometers covering the range of 2.5 to 25 μm wavelength are acceptable for oil spill analysis.

3.1 IR Operating Principle

Infrared Spectrophotometry deals with the vibrational and rotational energy modes between the atoms of molecules. The infrared spectrum of a particular molecule reflects the energy absorption pattern of these modes in the infrared region of the electromagnetic spectrum. Since each compound is constructed uniquely, the vibrational and rotational modes of a particular compound provide a spectral absorption pattern uniquely characteristic of that particular molecule. Although each compound has its own individual pattern distinct from any other, main structural features like functional groups and types of unsaturation display absorption bands at characteristic wavelengths allowing these functionalities to be determined as a general class.

3.2 Oil Spill Identification by IR

Kawahara has employed IR analysis to identify heavier petroleum products (greases, heavy residual [i.e., less volatile] fuel oil, and asphalt) (Ref. 7, 26). Since an oil spill sample is a mixture of various types of organic compounds, a qualitative and quantitative peak-by-peak correlation of an unknown sample against that of an authentic source sample is necessary as evidence for its identification.

Oil spill IR analysis normally involves liquids or solids. Liquids may be examined in solution or undiluted (neat). Viscous neat liquids are analyzed by pressing several mg between salt plates (e.g., NaCl, KBr) to form a sandwich cell. Mobile neat liquids also may be handled in cells from 0.1 to 1 mm in thickness (Ref. 7).

When solutions are used, the selection of solvent is important since the spectrum obtained from a solution is obliterated in wavelength regions where the solvent absorbs strongly. The solvent and sample must be dried with a drying agent (Na_2SO_4, $MgSO_4$, etc.) prior to placing in the cell to avoid permanent cell damage. Carbon tetrachloride, carbon disulfide, and chloroform are commonly used solvents.

Trace solution analyses are performed with microcavity cells equipped with a beam condenser. Cells having a path length of 0.05 mm and a capacity of 0.8 microliter are suitable. Solutions analyzed with matched cells must be dilute (10% maximum) to maintain compensation by the reference cell.

Solids are examined by grinding several mg of the solid with a drop of Nujol (mineral oil) and pressing into a thin film (mull) between salt plates (sandwich cell). Solids may also be examined as discs made from 1 mg of material ground and mixed with 100 mg of dried potassium bromide, then pressed in a die under pressure of about 30,000 lb per in^2.

As in GC and AA analysis it is essential to compare the oil spill sample with known suspect samples. Before an infrared spectrum is taken on a suitable infrared spectrophotometer, the chart must be aligned so that standard polystyrene absorption bands appear at the proper position. With IR analysis a peak-by-peak correlation is generally necessary for the entire spectrum. Loss of certain absorption bands may occur due to solubilization of certain components in the aqueous medium. Also, if the unknown has been exposed unduly to environmental factors, such as air, sunlight, or temperature (i.e., weathering), peroxidative and other chemical changes take place which alters the spectrum (Ref. 3, 19, 26, 27). Whatever absorption-band differences occur during weathering must then be rationalized on the basis of the chemical composition of the oil originally. Except for this aspect, which requires expert and perhaps ambiguous or controversial interpretation, IR analysis would enjoy a more important role in routine oil spill identification.

In order to minimize the effects of weathering on IR spectral identification capability, Kawahara (Ref. 7) recommends measurement of the absorbances at six IR frequencies (reciprocals of wavelengths): 350 cm^{-1}, 2925 cm^{-1}, 1600 cm^{-1}, 1375 cm^{-1}, 810 cm^{-1}, and 720 cm^{-1}. The ratio of the absorbance at one frequency to that at another frequency has been used to distinguish the type of pollutant as shown in Table 1(Ref. 28).

Mattson et al. (Ref. 27) report difficulties with the absorbance ratio method which may limit its utility: (a) extraction of oil pollution from associated extraneous solid matter (e.g., beach sand, debris, etc.) is necessary for IR transmission spectroscopy, but evaporation of the solvent after extraction sacrifices volatile organic components and changes the IR absorption ratio with respect to unextracted (neat) samples; (b) conventional use of sandwich cells (Ref. 7, 26) exposes the sample to heating in the spectrophotometer with concomittant component losses. For example, during a 30-min repetitive scan the absorption band at 720 cm^{-1} was reported (Ref. 25) to disappear while the band at 2925 cm^{-1} decreased by about 20%. This alters four

TABLE 1.

Characterization of Oil Pollutants According to IR Absorbance Ratios (Ref. 28)

	LUBE OIL	ASPHALT	NO. 6 FUEL OIL	NO. 5 FUEL OIL	CUTTER STOCK
$\frac{720\ cm^{-1}}{1375\ cm^{-1}}$	0.48	0.28	0.20	0.12	0.07
$\frac{3050\ cm^{-1}}{2925\ cm^{-1}}$	0.20	0.22	0.28	0.32	0.60
$\frac{1600\ cm^{-1}}{1375\ cm^{-1}}$	0.11	0.54	0.60	0.58	0.72
$\frac{1600\ cm^{-1}}{720\ cm^{-1}}$	0.24	2.05	3.27	5.00	10.20
$\frac{810\ cm^{-1}}{1375\ cm^{-1}}$	0.06	0.25	0.40	0.48	0.85
$\frac{810\ cm^{-1}}{720\ cm^{-1}}$	0.12	0.94	2.18	3.92	12.00

of the ratios used to distinguish the oil spill sample (Table 1, above). Mattson et al. conclude that IR methods involving direct heating of the oil sample prior to or during IR scanning should be avoided. Alternatively, Adlard (Ref. 19) suggests utilizing only a standard high-boiling fraction (e.g., bp 250°+C) for IR transmission spectroscopy. WOGA recommends using the 280°+C fraction (Ref. 22).

Mattson et al. (Ref. 27) discuss enhanced sensitivity inherent, with internal reflection IR spectroscopy. For example, oil pollution samples may be analyzed without extraction from extraneous associated solids. Also spectral alterations due to heating during IR scanning were implied to be minimized by the lower energy requirements of the internal reflectance method (for technical discussion see Ref. 19, 27).

Adlard (Ref. 19) presents an informative summary of role of IR analysis in oil spill identification, observing that if a full study of the complications to IR analysis due to oxidative weathering exists, it has not been published. In reference to the overall utility of IR spectrophotometry in identification of oil pollution, Adlard notes that most laboratories are already equipped with an IR spectrophotometer and that the time required to obtain a spectrum is comparatively short. Thus he concludes it is worthwhile to use IR analysis to supplement chromatographic and trace element (e.g., V/Ni) analyses.

4. Thin-Layer Chromatography (TLC)

TLC is a form of adsorption chromatography adapted to microanalytical applications (Ref. 29-32). It is widely used throughout organic chemical research in the analysis of nonvolatile compounds. TLC features speed, convenience and low cost. Sample separating capability and sensitivity in general is somewhat limited compared to GC.

4.1 TLC Operating Principle

Thin-layer chromatography is a form of liquid-solid chromatography in which relatively nonvolatile organic compounds dissolved in an organic solvent migrate along a thin layer of adsorbent solid. TLC embodies the same three basic chromatographic steps outlined in section 1.1. It differs from GC in that the mobile phase is a liquid, generally one or two of the common organic solvents, and the stationary phase is a finely powdered polar solid capable of interacting (associating) selectively with the organic sample components (solutes) on the basis of their comparative polarity. The rate of migration of a specific compound depends inversely on its comparative physicochemical affinity for the solvent (mobile) phase vs. the adsorbent (stationary) phase. The resolution or separation of similar compounds depends upon the chemical nature of the adsorbent, the thinness of the layer, the fineness of the adsorbent particle, and the choice of solvent(s).

TLC is practiced with a minimum of equipment. Chromatography takes place on glass or plastic plates coated with a thin layer of polar adsorbent, usually partially hydrated silica gel ($SiO_2 \cdot X\ H_2O$) or alumina ($Al_2O_3 \cdot X\ H_2O$) bound with an inert adhesive. A solution of the sample is spotted onto the adsorbent layer near one edge of the plate which is then placed on end in an air tight container (tank) provided with a shallow pool of developing solvent. The sample spot is placed near the solvent (within a few mm) but not in it. Capillary attraction causes the solvent in contact with the plate to rise upward along the plate carrying sample components in that direction. The ratio of the distance the sample components travel compared to the distance of the solvent front (R_f) depends upon the structure of the organic components, and the nature of the solvent (mobile phase) and the adsorbent (stationary phase) as described above. Commercially available TLC plates are 8 inches long. Typical solvents require 40 min to travel 6 in. which is a convenient point to terminate the chromatography by removing the plate from the tank. Solvent generally evaporates within minutes and the degree of non-volatile component separation can be assessed by viewing the plate under ultraviolet (UV) light, immersing in iodine (I_2) vapor, or spraying with specific color-developing (chromogenic) sprays. Laboratory practice for environmental applications is discussed in Reference 18.

4.2 Oil Spill Identification by TLC

Thin-layer chromatography (TLC) is geared to display specific, non-volatile compounds which are characteristic of petroleum and its products. The separation of such oil spill components is more according to chemical type than to individual compounds; however, particular compounds or classes of compounds may be highlighted in TLC analysis through use of specific color-developing (chromogenic) reagents or UV irradiation. Organic compounds which emit visible fluorescence when irradiated with UV light are particularly useful as marker compounds which are characteristic of petroleum and some of its products. The immense complexity of petroleum and some of its products may limit the value of TLC; however, this can be compensated for in part by the large variety of sample detecting (chromogenic) spray agents available (Ref. 29-32). By operating on a different principle of component separation and detection than GC, TLC offers an additional dimension of chromatographic analysis. Examples are given in Matthews (Ref. 33).

5. Summary and Recommendations

As previously noted, gas chromatography (GC) is the most generally useful technique to identify the source of aquatic oil pollution. GC can be applied to virtually all phases of organic constituent analysis, either alone or in conjunction with ancillary techniques such as distillation, selective solvent extraction and partition, adsorption chromatography, chemical derivatization or pyrolysis.

Analysis of the content of certain trace minerals, viz., vanadium and nickel, is a valuable complement to GC for source identification for reasons discussed above. Instrumentation for analysis of trace metallic elements is discussed under Metals (H2O-MET). Atomic absorption spectrophotometry (AA) is generally preferred over other techniques because of its comparative simplicity, freedom from interferences, and the fact that it is already widely used in water analysis laboratories.

Other instrumental techniques serve a supplemental function, e.g., thin-layer chromatography (TLC) with UV fluorescence detection and infrared spectroscopy (IR). TLC is fast and inexpensive but lacks rigor and definition for a primary role. IR is the subject of controversy, being neither satisfactorily defined nor widely accepted as a standard method (see above). The same is true of UV absorption and emission spectroscopy only more so (Ref. 19). Some of the techniques for measuring bulk properties mentioned earlier find use as supportive evidence for oil identification purposes; however their role is relatively minor.

5.1 GC Recommendations

GC analysis for the organic constituents of oil pollutants is a fairly demanding requirement due to the complex composition of typical oily samples. It is advisable that the GC instruments used for this task include the following features:

5.1.1 Temperature programming

Most manufacturers feature reasonably satisfactory temperature programming among their GC models. With the present forced-air GC ovens there are practical limits to temperature uniformity within the oven sapce. During isothermal operation, temperature gradients well under ±1°C are customary; however, during temperature programming, gradients within the oven unavoidably occur. Since sample component separation takes place within the GC column being heated (within the oven), some temperature lag from the intended program is inevitable. It is important that this be (a) minimal and (b) reproducible from chromatogram to chromatogram, thus one must compare instrument capabilities with care. Also, the choice of temperature programming rates varies according to manufacturer, so one must make certain that sufficient versatility is available, especially to simulate conditions used by others.

5.1.2 Flow Regulation

As with temperature programming, chromatogram reproducibility depends on carrier gas flow reproducibility and regulation. Most (but not all) GC manufacturers achieve flow regulation to within ±0.3%. The Brooks Division of Emerson Electric produces regulators which meet this specification. Other regulators not so precise may render inter-laboratory comparison of temperature-programmed chromatograms difficult. This is because the back pressure (resistance to flow) of the carrier gas increases with the temperature during programming, thus slowing the flow unless rigorously regulated. Also the carrier gas pneumatic system must be leak-free for precise flow regulation. This is best checked by the absence of growing bubbles in a soapy solution applied to various fitting seals when the instrument is cool. The septum through which the sample is introduced is the most likely place for a new leak to develop. It should be checked frequently and replaced when worn out.

5.1.3 Dual Columns

When used in the compensating mode, dual column GC minimizes the baseline deviation during temperature programmed chromatograms due to the background signal from stationary liquid phase bleed. The second (reference) column provides a sample-free background reference signal (from column bleed) to be subtracted from the sampling column signal. This actually isn't critical for mixtures as complex as petroleum and other oily contaminants because they already contribute a substantial apparent background from their envelope of unresolved components. Rather, the dual column configuration is better employed as two independent sampling columns for simultaneous analysis of two oil samples. Dual amplifiers are required (Ref. 34) and a second recorder is recommended over a dual pen recorder.

5.1.4 Capillary (1/16-in. O.D.) Columns

Packed GC columns are practical for general survey purposes in oil pollution analysis. The general nature of an unknown sample may be readily categorized on inexpensive 1/8-in. O.D. packed columns, 2 to 3-meters in length (Ref. 34). For final comparison to correlate the spill sample with known suspect samples, however, better GC columns (1/16-in. O.D.) are available and should be employed (see Fig. 2-7).

The 1/16-in. O.D. columns are commonly known as capillaries or open-tubular columns (see Discussion in part 1.2 above). The support-coated, open-tubular (SCOT) column is the most practical for oil spill analysis because small oil samples may be injected directly without sample attenuation. Because the expense of SCOT columns is several times that of the packed columns, it may be wise to attach a short, disposable section (e.g., 10-cm length) of 1/16-in. O.D., 0.065-in I.D., packed column between the injection/vaporization chamber and the SCOT column. This localizes residue build-up from undistilled oily samples on the short section of packed "pre-column" and minimizes permanent contamination of the more expensive SCOT column. Occasional backflushing of the SCOT column and replacement of the packed section of pre-column is advised for maintenance of good GC resolution.

5.1.5 Dual Detector Capability

In part 1.2 above the usefulness of carbon vs. sulfur detection (FID vs. FPD) in GC analysis of oil spill samples is discussed. To take advantage of this technique, which promises to become the cornerstone of oil spill analysis, it is essential that the gas chromatograph be either (a) supplied with a sulfur sensitive flame photometric detector (FPD) or (b) readily adaptable to its use. Instrumentation qualifying under either (a) or (b) is specifically discussed in the Instrument Notes.

5.2 AA Recommendations

AA spectrophotometry is recommended over other techniques (see below) for trace mineral analysis almost entirely on the basis that AA instrumentation is already in such wide usage in water quality analytical laboratories that additional outlay for vanadium (V) and nickel (Ni) trace analysis capability is mostly limited to the cost of the V and Ni hollow cathode lamps (ca. $100). It has been established that the trace concentrations of only V and Ni and their ratios are reliable for identifying an oil spill sample. This eliminates the need for broader spectrum trace metal analysis such as X-ray fluorescence, neutron activation, emission spectrography or spark source mass spectrography. Naturally, if such instrumentation is at hand, AA is not necessarily required for V and Ni analysis.

Owing to the trace levels of V and Ni encountered, a double beam AA spectrophotometer is recommended. Even then, ashing, selective solvent extraction and other enrichment procedures may be necessary to obtain sufficient accuracy. In this regard, the AA graphite furnace so significantly enhances the sensitivity that the foregoing time and attention consuming enrichment procedures may not be required.

5.3 TLC Recommendations

TLC is a relatively simple and inexpensive means to show consistency with oil spill identifications established by GC and AA and is recommended as a supportive technique. It is especially applicable to non-volatile, UV fluorescent organic components of the oil. Most commercially available TLC plates are satisfactory. A simple hand-held, long wavelength UV light ("mineral light" or "black light") obtainable from most laboratory supply houses is satisfactory for detection of fluorescent constituents.

5.4 IR and UV Recommendations

As Adlard has noted (Ref. 19), IR spectrophotometers are common in laboratories and the time and effort to make IR comparisons between an oil spill sample and suspect candidates is not great. Therefore, under these considerations IR should be utilized generally to support GC, AA and TLC evidence. Occasionally a case may arise in which the foregoing techniques may not yield clear results and the burden of proof of identity falls more heavily on IR comparisons. In this case it is recommended that IR comparisons be performed only on the nonvolatile fraction (e.g., bp 250°+C).

Ratios of IR absorbance at 6 different frequencies have been proposed to clarify the identity of oil spill samples; however, more complete evidence is needed before general acceptance can be anticipated. Also, weathering and other maltreatment of the oil spill sample may seriously compromise the effectiveness of IR comparison by eliminating certain absorption bands and/or creating artifact absorption bands. Purchase of IR spectrophotometeres solely for the purpose of identifying oil spills does not warrant a high priority.

At the present time it is recommended that UV irradiation be confined to use as a TLC fluorescence detector. UV has been described as a convenient and effective analytical tool for identifying oil spill samples, but upon further examination UV was found to be even more seriously compromised by weathering (sunlight, evaporation, oxygen, moisture, etc.) than IR analysis (Ref. 19). Hence UV absorption, emission or excitation spectroscopy may not be desirable as primary evidence except when the spill and comparison samples are known to be fresh.

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8. IDENTIFICATION INSTRUMENT NOTES

On the following pages are the Oil Identification Instrument Notes for those instruments currently commercially available. All instruments are laboratory type, including mobile laboratory applications. The descriptor in the mnemonic identifies the use as oil identification. The notes are arranged alphabetically by manufacturer and each model has been assigned a number.

The manufacturer's specifications have been published as available, and we gratefully acknowledge that all manufacturers have assisted in the compilation of their notes. All information has been supplied by the manufacturer, either from brochures and instruction manuals or by private communication with the manufacturer. If no information is given for a particular instrument specification, this indicates that none was available.

In order to assist the reader in determining which gas chromatographic instrumentation may be best suited for oil spill analysis, we have encouraged manufacturers to nominate a particular model from their product line which they (and we) believe best fulfills the sole purpose of oil spill identification. The reader will note that this generally indicates the least elaborate and expensive temperature programmed, dual column, dual FID, single amplifier (or electrometer, etc.) gas chromatograph. Because of possible additional analytical requirements discussed above, the gas chromatographs selected also generally include optional (at additional cost) accessories such as (a) a second, independent detector (FID or FPD) amplifier, (b) an independent flame photometric detector (FPD) for operation in conjunction with a flame ionization detector (FID), and (c) capillary column inlets, including adjustable inlet splitters. At present, it is not possible to determine precisely which of these GC accessory techniques will become accepted as standard equipment for oil spill analysis, therefore there is some advantage in having accessories available as options rather than as standard equipment; the user may incorporate them as desired. Other more expensive and elaborate instruments in a particular manufacturer's product line which offer additional pertinent standard or optional features are noted under "Remarks" near the end of the Instrument Note.

The Instrument Notes should not be used as separate entities in themselves. The reader should refer to the discussion preceeding the Instrument Notes, the referenced literature, and manufacturers' publications.

The technical information in these notes has been compiled from the best available sources and is believed to be correct and up-to-date. These notes will be continually updated, and additional information and comments are certainly solicited.

TABLE OF OIL IDENTIFICATION INSTRUMENTS

LABORATORY ANALYSIS

Principle of Operation	Instrument Note	Range*	Analysis Time	Cost	Multi-Parameter Capability	Remarks
GC-FID						
	Bendix 1	10^{-6} to 10^{-12}	20 to 60 min	$4200	FPD, ECD, TCD	Other Models Available
	Fisher 1	10^{-5} to 10^{-12}	"	$5600	"	"
	Hewlett Packard 1	10^{-5} to 10^{-11}	"	$4990	"	"
	Packard 1	10^{-6} to 10^{-12}	"	$4800	"	"
	Perkin-Elmer 1	10^{-5} to 10^{-12}	"	$5135	"	"
	Tracor 1	10^{-5} to 10^{-11}	"	$4455	"	"
	Varian 1	10^{-5} to 10^{-11}	"	$5140	"	"

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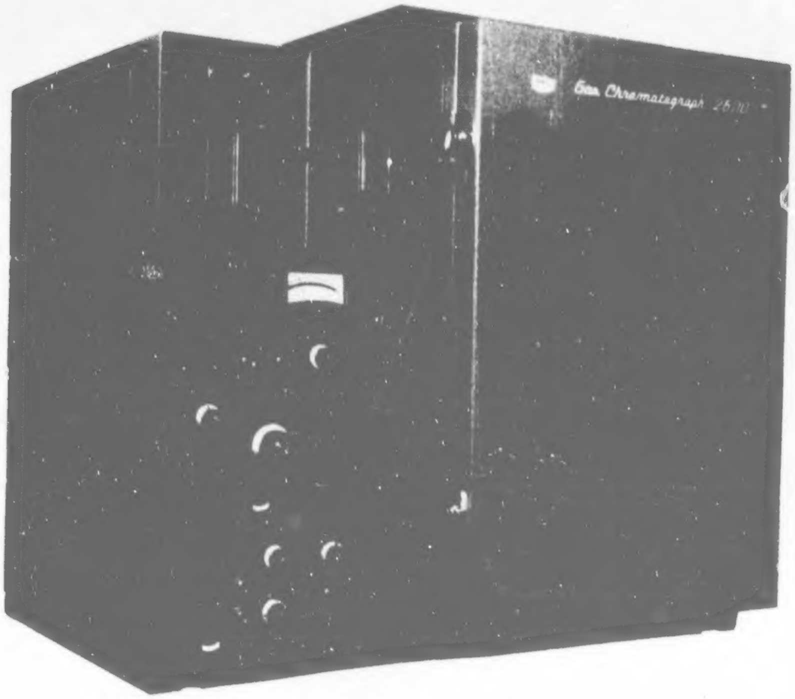
*g/sec Hydrocarbon

Oil/Grease Analyzer

Gas Chromatograph Model 2625-06-002



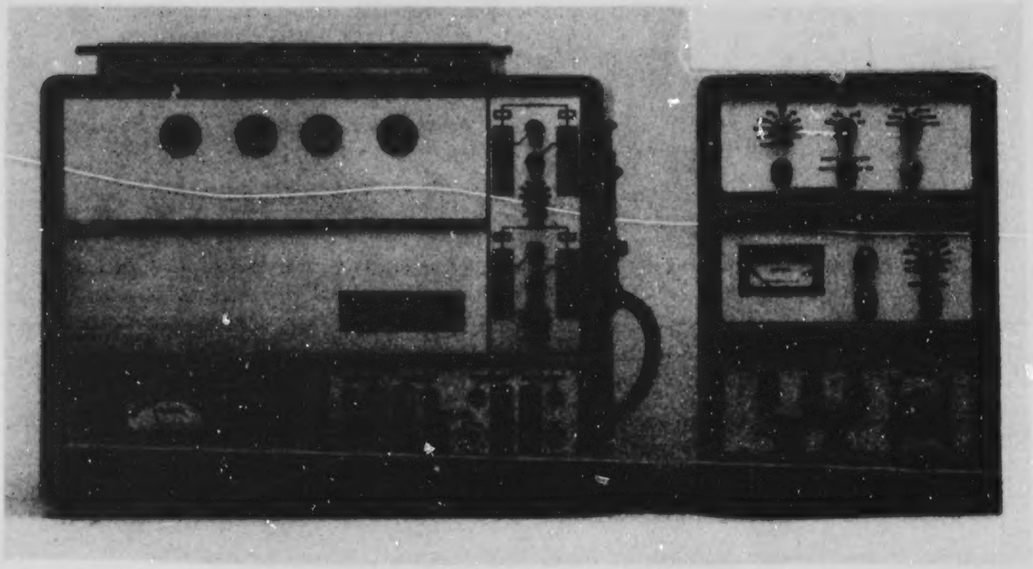
Class	Laboratory: routine analysis/research
Principle of Operation	Gas Chromatography-Flame Ionization Detection (GC-FID)
Sensitivity	2×10^{-12} g/sec hydrocarbon (0.01 coulombs/g carbon)
Range	10^{-6} to 10^{-12} g/sec hydrocarbon
Interferences	Appreciable interferences from: organic compounds in general Moderate interferences from: GC column and septum bleed Slight or no interferences from: H_2O, CO_2, CO, COS, CS_2, SO_2, N_2, Ar, He, Ne, among others
Multiparameter Capability	Convertible by manufacturer's representative to: electron capture detection (ECD) for analysis of halogenated hydrocarbons (pesticides), thermal conductivity detection (TCD) for gas analysis (sewage digester gas), flame photometric detection (FPD) for sulfur analysis
Sampling	Method: Syringe injected aliquot of separated oil or grease or organic solvent extract of water sample
Sample Inlet	Type: Silicone rubber septa, screw-cap retained on stainless-steel injection ports 1/4", 1/8", 3/16" sizes standard On-Column Injection: Available in 1/4" Glass Liners (Inserts): Available in 1/4", 1/8", 3/16" sizes Capillary Columns: Accessory stream-splitting injection port available for use with 1/16" tubing; variable ratios available up to 200/1

Sample Inlet (Continued)	Temperature Range: Ambient to 500°C Temperature Regulation: Fully proportional, ±0.5°C Overheat Protection: Line fuse only
Column Oven	Type: Dual columns, injection ports and detectors; metal or glass columns, vertically coiled; thermostatted, forced air circulation Carrier Gas: He or N_2, prepurified Flow Control: Independent differential flow regulators Flow Range, Tolerance: 2 to 200 cc/min He, ±0.3% Flow Calibration: Dual rotameters standard, calibrated for He Column Capacity: Standard, 1/8" O.D. metal tubing, 2 ea.: 50' + Optional, 1/4" O.D. metal tubing, 2 ea.: 30' + Accessory, 1/16" O.D. metal capillary, 2 ea.: ca. 300' + Temperature Range: Continuously adjustable, ambient to 500°C Temperature Regulation: Fully proportional, ±0.5°C Overheat Protection: Variable bimetallic cutoff switch Temperature Program: 20 linear rates, 0.25, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 16, 20, 24, 28, 32, 36, 40 Initial Isothermal Timer: Available on automatic cycle accessory programmer Final Isothermal Timer: Cooling Rate: 250°C to ambient in 2 min
Detector	Type: Independent or compensating dual flame ionization (FID) Temperature Range: Ambient to 500°C Temperature Regulation: Fully proportional, ±0.5°C Overheat Protection: Optional bimetallic cutoff switch Accessory Gas Flow: Ca. 30 cc/min prepurified H_2; ca. 300 cc/min prepurified air per FID Linear Dynamic Range: Greater than 10^6
Detector Amplifier	Type: Solid state, F.E.T. input design, single differential channel, dual channel optional Sensitivity: 1×10^{-12} A full scale Linear Dynamic Range: 10^6 Drift: 1×10^{-13}A/da at constant ambient Noise: Less than 1×10^{-14} A Background Suppression: 0 to $\pm 10^{-11}$, 10^{-8} A with coarse and fine adjustment Attenuation: X1, X10, X100, . . . X100,000 Outputs: For 1mV: for integrator or computer 1 V Time Constant: 0.22 sec maximum
Requirements	Recorder: 1 mV, servo-type, strip chart Pressure Regulated Gas Supplies: 0 to 60 psig He; 0 to 25 psig H_2; 0 to 60 psig air; all gases, prepurified grade Power: 117 V, 60 Hz (220 or 206 V, 50 Hz optional); 3000 W maximum Size: 63.7 cm H, 68.8 cm W, 53.4 cm D (25" x 27" x 21") Weight: 135 kg (300 lb)
References	Manufacturer's catalog, "Gas Chromatography"
Features	Optional dual independent FID amplifiers (+ $525), flame photometric detector (FPD) also available for simultaneous operation with FID

Cost	Gas chromatograph model 2625-2	$4200
Remarks	Standard, independent FID vs FPD available in Bendix Model 2603 ($7035).	
Address	Bendix Corporation, Process Instruments Division P.O. Drawer 831 Lewisberg, WV 24901 (304) 647-4358	

Oil/Grease Analyzer

Gas Chromatograph Model 4802-100

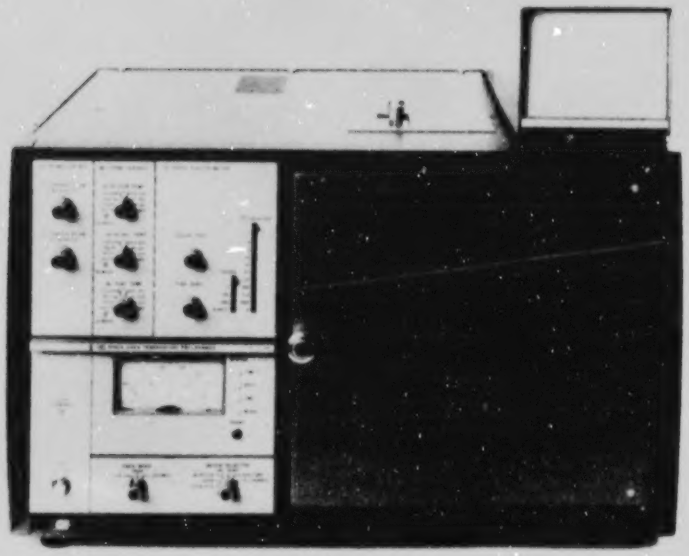


Class	Laboratory: Routine analysis/research
Principle of Operation	Gas Chromatography-Flame Ionization Detection (GC-FID)
Sensitivity	5×10^{-12} g/sec hydrocarbon (0.015 coulombs/g carbon)
Range	10^{-5} to 10^{-12} g/sec hydrocarbon
Interferences	Appreciable interferences from organic compounds in general Moderate interferences from GC column and septum bleed Slight or no interferences from H_2O, CO_2, CO, COS, CS_2, SO_2, N_2, Ar, He, Ne, among others
Multiparameter Capability	Convertible by manufacturer's representative to electron capture detection (ECD) for analysis of halogenated hydrocarbons (pesticides), thermal conductivity detection (TCD) for gas analysis (sewage digester gas), flame photometric detection (FPD) for sulfur, phosphorus analysis
Sampling	Method: Syringe injected aliquot of separated oil or grease or organic solvent extract of water sample
Sample Inlet	Type: Silicone rubber septa, screw-cap retained on stainless-steel injection ports, 1/8" size (standard); 1/4" size (optional) On-column injection: Available in 1/8" and 1/4" glass and 1/8" metal Glass liners (inserts): Available in 1/4" size only Capillary columns: Accessory stream-splitting injection port available for use with 1/16" tubing; various fixed-split ratios available (e.g., 5:1 to 1000:1) Temperature range: 50° to 450°C Temperature regulation: Fully proportional, ±0.5°C Overheat protection: Line fuse only

Column Oven	Type: Dual columns, injection ports and detectors; metal or glass columns, vertically coiled; thermostatted, forced air circulation Carrier gas: He or N_2, prepurified Flow control: independent differential flow regulators Flow range, tolerance: 2 to 200 cc/min He, ±0.3% Flow calibration: 2 rotameters, graduations uncalibrated for He Column capacity: Standard, 1/8" O.D. metal tubing, 2 ea.: 100' Optional, 1/4" O.D. metal tubing, 2 ea.: 50' Accessory, 1/16" O.D. metal capillary, 2 ea.: ca. 300' + Temperature range: Continuously adjustable, ambient to 400°C Temperature regulation: Fully proportional, ±0.5°C Overheat protection: 400°C cut-off, fusible metal strip; and adjustable limit switch Temperature program: 120 linear rates, 0° to 59.5°C/min in 0.5°/min steps Initial isothermal timer: 0 to 99 min in 1 min steps Final isothermal timer: 0 to 89 min in 1 min steps, also ∞ Cooling rate: 400° to 75°C in 10 min with main door closed
Detector	Type: Independent or compensating dual flame ionization (FID) Temperature range: 50° to 400°C Temperature regulation: Fully proportional, ±0.5°C Overheat protection: Fuse Accessory gas flow: ca. 30 cc/min prepurified H_2; ca. 300 cc/min prepurified air per FID Linear dynamic range: Greater than 10^7
Detector Amplifier	Type: Varacter bridge electrometer, single or dual channel Sensitivity: 1×10^{-12} A full scale Linear dynamic range: 10^6 Drift: 0.3%/hr at constant ambient Noise: 1.5% peak to peak at maximum sensitivity with cable disconnected Background suppression: 0 to $\pm 10^{-7}$ A with coarse and fine adjustment Attenuation: Input (range), X1, X10, X100, X1,000 Output (attenuator), X1, X2, X4,... X8196 Outputs: For recorder, 1, 10 mV; for integrator or computer, 1, 10 V Time constant: 0.3 sec maximum
Requirements	Pressure regulated gas supplies: 0 to 80 psig He; 0 to 40 psig H_2; 0 to 80 psig air; all gases, prepurified grade Power: 117 V, 60 Hz (220 V, 50 Hz optional); 3000 W maximum Size: 56 cm H, 100 cm W, 53.1 cm D (22-1/8" x 39-1/2" x 21") Weight: 159 kg (350 lb)
References	a.) Manufacturer's Bulletin No. 271 (U.S./Can.) 11-102-100
Features	Optional flame photometric detector (FPD) for simultaneous operation with FID, optional independent dual FID amplifiers
Cost	Gas chromatograph model 4802-100 $5600
Remarks	Model 4804-200 ($8600) has dual independent FID amplifiers and 4-column oven (e.g., for dual packed column/dual capillary column capability); optional FPD for simultaneous operation with FID
Address	Analytical Instrument Division Fisher Scientific Company 711 Forbes Avenue Pittsburgh, PA 15219 (412) 562-8300 Telex 86839

Oil/Grease Analyzer

Gas Chromatograph Model 5711A



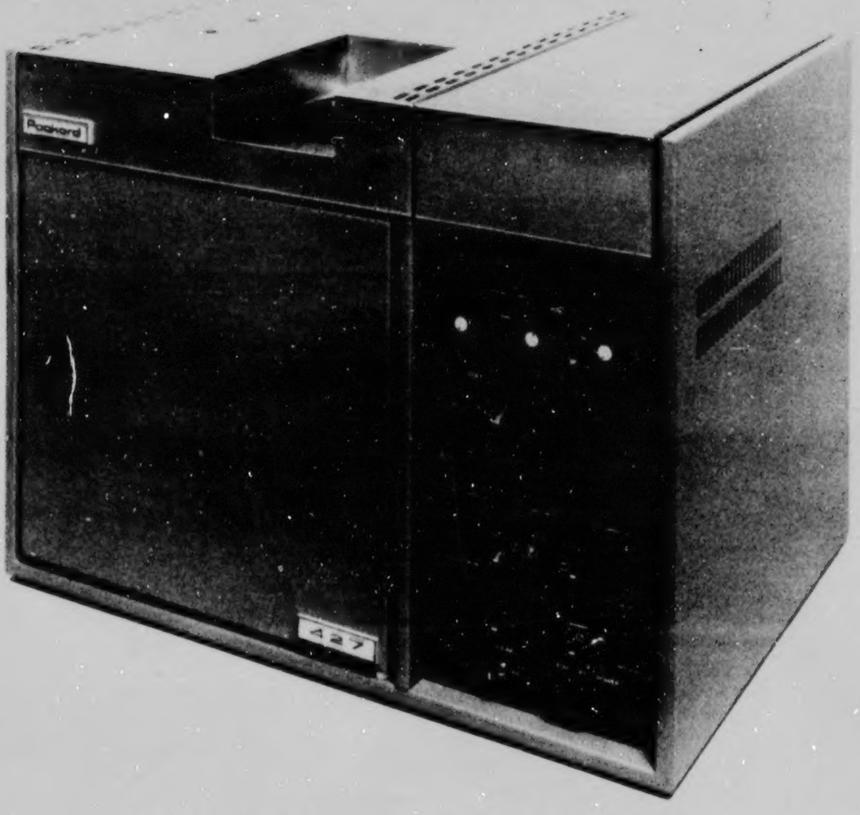
Class	Laboratory: Routine analysis/research
Principle of Operation	Gas Chromatography-Flame Ionization Detection (GC-FID)
Sensitivity	5×10^{-12} g/sec hydrocarbon (0.015 coulombs/g carbon) minimum
Range	10^{-5} to 10^{-11} g/sec hydrocarbon
Interferences	Appreciable interferences from organic compounds in general Moderate interferences from GC column and septum bleed Slight or no interferences from H_2O, CO_2, CO, COS, CS_2, SO_2, N_2, Ar, He, Ne, among others
Multiparameter Capability	Convertible by manufacturer's representative to electron capture detection (ECD) for analysis of halogenated hydrocarbons (pesticides); thermal conductivity detection (TCD) for gas analysis (sewage digester gas), flame photometric detection (FPD) for sulfur analysis
Sampling	Method: Syringe injected aliquot of separated oil or grease or organic solvent extract of water sample
Sample Inlet	Type: Silicone rubber septa, screw-cap retained on stainless-steel injection ports, 1/8" or 1/4" sizes On-column injection: Available in 1/8" and 1/4" sizes Glass Liners (inserts): Available in 1/4" size Capillary columns: Accessory stream-splitting injection port available for use with 1/16" tubing; split ratios available, 10:1 to 2000:1
	Temperature range: 100° to 400°C in 50° steps Temperature regulation: Fully proportional, ±0.5°C Overheat protection: fail-safe circuitry, line fuse

Column Oven	Type: Dual columns, injection ports and detectors; metal or glass columns, vertically coiled; thermostatted, forced air circulation Carrier gas: He or N_2, prepurified Flow control: independent differential flow regulators; Flow range, tolerance: 2 to 200 cc/min He, ±0.3% Flow calibration: soap bubble flowmeter (rotameters optional) Column capacity: Standard, 1/8" O.D. metal tubing, 2 ea.: 30' Optional, 1/4" O.D. metal tubing, 2 ea.: 15' Optional Accessory, 1/16" O.D. metal capillary, 2 ea.: ca. 100' Temperature range: Continuously adjustable, ambient to 400°C Temperature regulation: Fully proportional, ±0.5°C Overheat protection: independent control circuit to protect against thermal runaway Temperature program: 6 linear rates, 1, 2, 4, 8, 16, 32°C/min Initial isothermal timer: 0, 1, 2, 4, 8, 16, 32, ∞ min Final isothermal timer: 0, 1, 2, 4, 8, 16, 32, ∞ min Co-ling rate:
Detector	Type: Dual independent or differential flame ionization (FID) Temperature range: 100° to 400°C in 50° steps Temperature regulation: Fully proportional, ±0.5°C Overheat protection: fail-safe circuitry, line fuse Accessory gas flow: ca. 30 cc/min prepurified H_2; ca. 240 cc/min prepurified air per FID Linear dynamic range: Greater than 10^7, ±4% linearity
Detector Amplifier	Type: Solid state two-stage, single channel Sensitivity: 5×10^{-12} A full scale Linear dynamic range: greater than 10^6 on all ranges Drift: 4×10^{-14} A/hr @ constant ambient Noise: 1×10^{-14} A with input capped Background suppression: 0 to $\pm 10^{-6}$ A with coarse and fine adjustment Attenuation: Input (range), X1, X10, X100, X1000, remote capability Output (attenuator), X1, X2, X4,...X1024 Outputs: For recorder, 1 mV; for integrator, 1 V; for computer, 10 V Time Constant: 1 sec maximum, less than 0.5 sec nominal
Requirements	Pressure regulated gas supplies: 0 to 60 psig He; 0 to 40 psig H_2; 0 to 60 psig air; all gases, prepurified grade Power: 117 V, 60 Hz (220 V, 50 Hz optional); 1800 W maximum Size: 46.9 cm H, 56.2 cm W, 48.1 cm D (18-1/2" x 22-1/4" x 19") Weight: 37 kg (85 lb)
References	a) Manufacturer's bulletin for 5700 series b) Manufacturer's catalog: Analytical Instruments for Chemistry (1975)
Features	Optional flame photometric detector available
Cost	Gas chromatograph Model 5711A $4990
Remarks	Model 5731A ($5450) has standard independent dual FID amplifiers, and optional FPD, TCD, ECD, TID
Address	Hewlett-Packard Analytical Instruments Route 41 Avondale, PA 19311 (215) 268-2281; TWX 510-663-8268

H2O-OIL
Oil Identification
Packard 1
Aug. 1975

Oil/Grease Analyzer

Gas Chromatograph Model 427



Class	Laboratory: Routine analysis/research
Principle of Operation	Gas Chromatograph-Flame Ionization Detection (GC-FID)
Sensitivity	1 x 10^{-12} g/sec hydrocarbon (0.020 coulombs/g carbon)
Range	10^{-6} to 10^{-12} g/sec hydrocarbon
Interferences	Appreciable interferences from: organic compounds in general Moderate interferences from: GC column and septum bleed Slight or no interferences from: H_2O, CO_2, CO, COS, CS_2, SO_2, N_2, Ar, He, Ne, among others
Multiparameter Capability	Convertible by manufacturer's representative to: electron capture detection (ECD) for analysis of halogenated hydrocarbons (pesticides), thermal conductivity detection (TCD) for gas analysis (sewage digester gas); flame photometric detection (FPD) for sulfur analysis will be available.
Sampling	Method: Syringe injected aliquot of separated oil or grease or organic solvent extract of water sample

Sample Inlet

Type: Silicone rubber septa, screw-cap retained on 1/8" and 1/4" standard stainless-steel injection ports, also 6 mm glass column port
On-Column Injection: Standard for 1/4" or 1/8" columns.
Glass Liners (Inserts): Available in 1/4" size, adaptable to 1/8"
Capillary Columns: Accessory stream-splitting injection port available for use with 1/16" tubing; 1 fixed-split ratio available, 100/1, other ratios possible

Temperature Range: 0° to 500°C in 10°C steps
Temperature Regulation: Proportional integral differential ± 0.5% of set point.
Overheat Protection: Fail safe circuitry

Column Oven

Type: Dual columns, injection ports and detectors; metal or glass columns, vertically coiled; thermostatted, forced air circulation
Carrier Gas: He or N_2, prepurified
  Flow Control: Independent differential flow regulators
  Flow Range, Tolerance: 2 to 100 cc/min He, ±0.1%
  Flow Calibration: soap bubble flowmeter(on-column pressure gauges)

Column Capacity: Standard, 1/8" O.D. metal tubing, 2 ea.: 12 m
  " 1/4" O.D. metal tubing, 2 ea.: 4 m
  Accessory, 1/16" O.D. metal capillary, 2 ea.: ca. 100 m
Temperature Range: Ambient to 499°C in 1°C steps

Temperature Regulation: Proportional integral differential, ± 0.02°C.
Overheat Protection: Fail safe circuitry
Temperature Program: 40 linear rates, 1 to 39° in 1° steps

Initial Isothermal Timer: 0 to 99 min in 1 min steps
Final Isothermal Timer: 0 to 99 min in 1 min steps
Cooling Rate: from 400°C to 100°C in 13 minutes
  200°C to 100°C in 8 minutes

Detector

Type: Independent or compensating dual flame ionization (FID)
Temperature Range: Ambient to 400°C
Temperature Regulation: Fully proportional, ±0.1°C
Overheat Protection: Fail safe circuitry
Accessory Gas Flow: ca. 30 cc/min prepurified H_2; ca. 300 cc/min prepurified air per FID
Linear Dynamic Range: 10^6

Detector Amplifier

Type: Solid state, parametric, single channel
Sensitivity: 2.0×10^{-12} A full scale
Linear Dynamic Range: 10^7 overall, including ranging

Drift: Less than 10^{-14}A/48hr at constant ambient

Noise: 0.5×10^{-14} A
Background Suppression: 0 to ± 10^{-8} A maximum.
Attenuation: Input (range), X1, X10, X100
  Output (attenuator), X1, X2, X4, . . . X1024
Outputs: For recorder 1, 10 mV for integrator and computer IV

Time Constant: 0.6 sec. max.

Requirements

Recorder: 1 mV, servo-type, strip chart
Pressure Regulated Gas Supplies: 0 to 100 psig He; 0 to 60 psig H_2; 0 to 60 psig air; all gases, prepurified grade
Power: 117 V, 60 Hz (220 V, 50 Hz optional); 1KVA maximum
Size: 40 54 41 (16" × 22" × 16")
Weight: 37 kg (82 lb)

Reference	Manufacturer's brochure no. 1208
Features	Dual FID; low pressure regulators for carrier gas, air and hydrogen supplies; automatic cooldown
Cost	Gas chromatograph model 427 dual FID, programmed with autocool $4800
Remarks	Model 417 also available
Address	Packard Instrument Co. 2200 Warrenville Rd. Downers Grove, IL 60515 (312) 969-6000 Telex 72-8378 TWX 910/695-3220

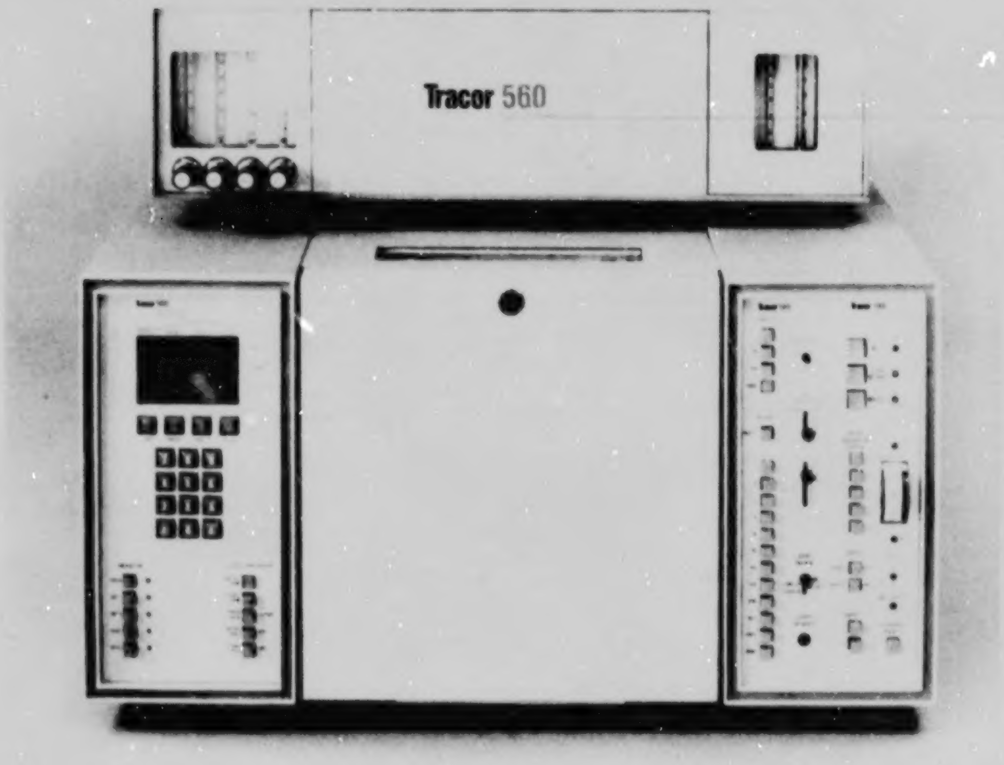
Oil/Grease Analyzer
Gas Chromatograph Model 3920 B (Option 045-0314)

Class	Laboratory: Routine analysis/research
Principle of Operation	Gas Chromatography-Flame Ionization Detection (GC-FID)
Sensitivity	5×10^{-12} g/sec hydrocarbon (0.015 coulombs/g carbon)
Range	10^{-5} to 10^{-12} g/sec hydrocarbon
Interferences	Appreciable interferences from organic compounds in general. Moderate interferences from GC column. Slight or no interferences from H_2O, CO_2, CO, COS, CS_2, SO_2, N_2, Ar, He and Ne, among others.
Multiparameter Capability	Convertible by manufacturer's representative to electron capture detection (ECD) for analysis of halogenated hydrocarbons (pesticides); thermal conductivity detection (TCD) for gas analysis (sewage digester gas); nitrogen/phosphorus detector for selective response to nitrogen and phosphorus compounds (carbamate and organophosphorus pesticides); Flame Photometric Detection (FPD) for selective response to phosphorus or sulfur compounds (pesticides, sulfur in oil).
Sampling	Method: Syringe injected aliquot of separated oil or grease or organic solvent extract of water sample
Sample Inlet	Type: Silicone rubber septa, screw-cap retained on interchangeable stainless-steel injection ports, 1/8" or 1/4" sizes On-Column Injection: Available in 1/8" and 1/4" sizes Glass Liners (Inserts): Available in 1/8" and 1/4" sizes Capillary Columns: Accessory stream-splitting injection ports, metal or all-glass for use with metal or all-glass capillary columns

Sample Inlet	Temperature Range: Continuously adjustable, 50° to 400°C Temperature Regulation: Fully proportional, ±1% Overheat Protection: Diode overcurrent limiting protector
Column Oven	Type: Dual columns, injection ports and detectors; glass or metal columns, horizontally coiled; thermostatted, forced air circulation Carrier Gas: Helium or nitrogen Optional Flow Control: independent differential flow controllers Flow Range, Tolerance: 2 to 200 cc/min He, ±0.3% Flow Calibration: Soap bubble flowmeter; optional direct setting flow controllers Column Capacity: Standard, 1/8" O.D. metal tubing, 2 ea.: 52' Optional, 1/4" O.D. metal tubing, 2 ea.: 24' Accessory, 1/16" O.D. metal capillary, 2 ea.: ca 600' Temperature Range: Continuously adjustable, ambient to 400°C at 1° intervals Temperature Regulation: Fully proportional, ±0.5°C Overheat Protection: Cutoff circuitry adjusted for 30°C above set-point temperature program: 7 linear rates, 0.5, 1, 2, 4, 8, 16, 32°C/min Initial Isothermal Timer: 0, 1, 2, 4, 8, 16, 32, 64 min Final Isothermal Timer: 0, 1, 2, 4, 8, 16, 32, 64, ∞ min Cooling Rate: Temperature dependent
Detector	Type: Independent or compensating dual flame ionization (FID) Temperature Range: Continuously adjustable, 50° to 400°C Temperature Regulation: Fully proportional, ±1°C Overheat Protection: Diode overcurrent limiting protector Accessory Gas Flow: ca. 40 cc/min prepurified H_2; ca. 600 cc/min prepurified air Linear Dynamic Range: Greater than 10^6
Detector Amplifier	Type: Solid state design, single or differential input Sensitivity: 5×10^{-12}, a full scale Linear Dynamic Range: 10^6 Drift: Less than 3×10^{-14} A/wk at constant ambient temperature and line voltage; less than 0.3%/°C with cables connected Noise: 3×10^{-14}A, with detector cable Background Suppression: 0 to $\pm 2 \times 10^{-8}$ A with coarse and fine adjustment Attenuation: Input (range), X1, X10, X100, X1000 Output (attenuator), X1, X2, X4, ... X1024 Outputs: For recorders, 1, 2.5, 5mV; for electronic integrators 1V; for computers 10V Time Constant: 0.15 sec maximum, 0.03 sec nominal
Requirements	Pressure Regulated Gas Supplies: 0 to 80 psig He; 0 to 25 psig H_2; 0 to 100 psig air; all gases prepurified grade Recorder: 1 mV, servo type, strip chart Power: 117 V, 60 Hz (220 V, 50 Hz optional); 2200 maximum Size: 45.7 cm H, 72.2 cm W, 55.9 cm D (18" × 28" × 22") Weight: 91 kg (200 lbs)
Features	Convertible to ECD, FPD, TCD, N/PD; optional amplifier (045-0168) provides independent, simultaneous operation of dual FID
References	Manufacturer's bulletin No. L-166 and letter of September 12, 1975
Cost	Gas Chromatograph Model 3920B (045-0314) $5,135.
Remarks	Model 910 gas chromatographs similar but feature computer or punch card control
Address	Perkin-Elmer Corporation Instrument Division Norwalk, CT 06852 (203)762-4811 Cable: PECO-NORWALK

Oil/Grease Analyzer

Gas Chromatograph Model 113550-4201-1200-3102-220



Class	Laboratory: routine analysis/research
Principle of Operation	Gas Chromatography-Flame Ionization Detection (GC-FID)
Sensitivity	1×10^{-11} g/sec hydrocarbon
Range	10^{-5} to 10^{-11} g/sec hydrocarbon
Interferences	Appreciable interferences from: organic compounds in general Moderate interferences from: GC column and septum bleed Slight or no interferences from: H_2O, CO_2, CO, COS, CS_2, SO_2, N_2, Ar, He, among others
Multiparameter Capability	Convertible by manufacturer's representative to: electron capture detection (ECD) for analysis of halogenated hydrocarbons (pesticides), thermal conductivity detection (TCD) for gas analysis (sewage digester gas), flame photometric detector (FPD) for sulfur analysis, Coulson conductivity detector (CCD) specific for analysis of nitrogen or sulfur
Sampling	Method: Syringe injected aliquot of separated oil or grease or organic solvent extract of water sample

Sample Inlet

Type: Silicone rubber septa, screw-cap retained on glass or stainless-steel injection ports
On-Column Injection: Available in 1/16", 1/8", and 1/4" sizes
Glass Liners (Inserts): Available in 1/8" and 1/4" size
Capillary Columns: Accessory steam-splitting injection port available for use with 1/16" tubing; variable split ratios available

Temperature Range: Ambient to 450°C
Temperature Regulation: Solid state, thermocouple feedback
Overheat Protection: 420°C; Open thermocouple detection

Column Oven

Type: Dual columns, injection ports and detectors; metal or glass columns, vertically coiled; thermostatted, forced air circulation
Carrier Gas: He or N_2, prepurified
Flow control: independent differential flow regulators
Flow range, tolerance: 2 to 200 cc/min He, ±0.3%
Flow calibration: soap bubble flow meter standard, rotameters optional
Column Capacity: Standard, 1/8" O.D. metal tubing, 2 ea.: 60'
Optional, 1/4" O.D. metal tubing, 2 ea.: 30'
Accessory, 1/16" O.D. metal capillary, 2 ea.: ca. 200'
Temperature Range: Continuously adjustable, ambient to 400°C

Temperature Regulation: Fully proportional ±0.25°C
Overheat Protection: Adjustable oven overheat protection 199°C, 299°C or 399°C with internal lock-out preventing operator error setting temp. above 400°C thermocouple open circut detection
Temperature Program: 1 to 50° /C in 1° steps
Initial Isothermal Timer: 0-999 min in 1 min increments
Final Isothermal Timer: 0-999 min in 1 min increments

Detector

Type: Independent or compensating dual flame ionization (FID)
Temperature Range: Ambient to 400°C
Temperature Regulation: Solid state thermocouple feedback
Overheat Protection: 420°C; open thermocouple detection
Accessory Gas Flow: ca. 30 cc/min prepurified H_2; ca. 180 cc/min prepurified air per FID
Linear Dynamic Range: Greater than 10^7

Detector Amplifier

Type: Solid state, parametric design, single or dual channel
Sensitivity: 5×10^{-12} A full scale with lmv recorder
Linear Dynamic Range: 10^7

Drift: 1%/day at constant ambient

Noise: 1×10^{-14} A
Background Suppression: Three ranges, 0 to $\pm 10^{-6}$, 10^{-8}, 10^{-10} A with corase and fine adjustment
Attenuation: Input (range), X1, X10, X100, . . . X1,000,000
Output (attenuator), X1, X2, X4, . . . X1024; Auto attenuation optional
Outputs: For recorder, lmV; for computer 1V, 10V

Time Constant: 0.3 sec maximum

Requirements

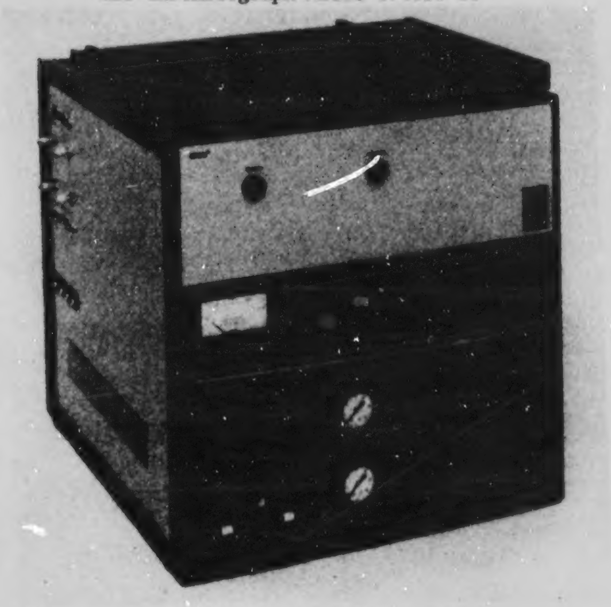
Recorder: 1 mV, servo-type, strip chart
Pressure Regulated Gas Supplies: 0 to 40 psig He; 0 to 25 psig H_2; 0 to 100 psig air; all gases, prepurified grade
Power: 117 V, 60 Hz or 220V, 50Hz
Size: 63.5 cm W x 41.2 cm D x 52.5 cm H (25" x 16" x 20")
Weight: 50 kg (110 lbs)
Power Consumption: 2250 Watts Max.

Features	Dual independent FID amplifiers standard, optional flame photometric detector (FPD) for simultaneous operation with FID
Cost	Gas Chromatograph Model 114800-4212-0003-3102-2100-5002-5102-1200-3102-2200 $4,455.00
Remarks	Model 114800-4212-0003-3100-3400-2200-5002-5202 ($7,145.00) has standard independent, simultaneous FID and FPD detection
Address	Tracor Analytical Instruments 6500 Tracor Lane Austin, TX 78721 (512) 926-2800 TWX 910-874-1372 Cable TRACOR

H2O-OIL
Oil/Identification
Varian Aerograph 1
Sept. 1975

Oil/Grease Analyzer

Gas Chromatograph Model 274030-00



Class	Laboratory: Routine analysis/research
Principle of Operation	Gas Chromatography-Flame Ionization Detection (GC-FID)
Sensitivity	1×10^{-12} g/sec hydrocarbon (0.01 coulombs/g carbon)
Range	10^{-5} to 10^{-11} g/sec hydrocarbon
Interferences	Appreciable interferences from organic compounds in general Moderate interferences from GC column and septum bleed Slight or no interferences from H_2O, CO_2, CO, COS, CS_2, SO_2, N_2, Ar, He, Ne, among others
Multiparameter Capability	Convertible by manufacturer's representative to electron capture detection (ECD) for analysis of halogenated hydrocarbons (pesticides); thermal conductivity detection (TCD) for gas analysis (sewage digester gas); thermionic (alkali flame) detection (organic phosphorus or nitrogen, e.g. pesticides)
Sampling	Method: Syringe injected aliquot of separated oil or grease or organic solvent extract of water sample
Sample Inlet	Type: Silicone rubber septa, screw-cap retained on stainless-steel injection ports, 1/4" size (standard) On-column injection: Available in 1/4" size Glass liners (inserts): Available in 1/4" size Capillary columns: Accessory stream-splitting injection port available for use with 1/16" tubing: variable split ratio available, 0 to 300/1 Temperature range: Ambient to 400°C Temperature regulation: Manually adjustable potentiometer Overheat protection: line fuse only

Column Oven

Type: Dual columns, injection ports and detectors; metal or glass columns, vertically coiled; thermostatted, forced air circulation
Carrier gas: He or N_2, prepurified
  Flow control: independent differential flow regulators;
  Flow range, tolerance: 10 to 150 cc/min He, ±1%
  Flow calibration: soap bubble flowmeter
Column capacity:
  Standard, 1/8" O.D. metal tubing, 2 ea.: 100'
  Optional, 1/4" O.D. metal tubing, 2 ea.: 50'
  Accessory, 1/16" O.D. metal capillary, 2 ea.: ca. 150'
Temperature range: Continuously adjustable, ambient to 400°C

Temperature regulation: Fully proportional, ±0.5°C
Overheat protection: Variable bimetallic temperature limit switch
Temperature program: 10 linear rates, 0.5, 1, 2, 4, 6, 8, 10, 12, 15, 20°C/min
Initial isothermal timer: 0 to 99 min in 1 min steps
Final isothermal timer: 0 to 99 min in 1 min steps
Cooling rate: 50°C/min

Detector

Type: Independent or compensating dual flame ionization (FID)
Temperature range: Ambient to 400°C
Temperature regulation: Fully proportional, ±0.5°C
Overheat protection: Optional temperature limit switch
Accessory gas flow: ca. 30 cc/min prepurified H_2; ca. 350 cc/min prepurified air per FID
Linear dynamic range: Greater than 10^6

Detector Amplifier

Type: Solid state, dual matched F.E.T. (dual channel)
Sensitivity: 1×10^{-12} A full scale
Linear dynamic range: 10^5

Drift: Less than 1%/mo @ constant ambient

Noise: Less than 1×10^{-14} A
Background suppression: 0 to $\pm 9 \times 10^{-10}$ A with coarse and fine adjustment
Attenuation: Input (range), X1, X10, X100, X1000
  Output (attenuator), X1, X2, X4,...X1024
Outputs: For recorder 1 mV; for integrator, computer, 1 V

Time constant: 0.3 sec maximum

Requirements

Pressure regulated gas supplies: 0 to 65 psig He; 0 to 25 psig H_2; 0 to 100 psig air; all gases, prepurified grade
Power: 117 V, 60 Hz (220 V, 50 Hz optional); 1700 W maximum
Size: 55.6 cm H, 49.5 cm W, 54.6 cm D (22" x 19-1/2" x 21-1/2")
Weight: 59 Kg (130 lbs)

References

a.) Manufacturer's Catalog, 1971 Instruments and Accessories

Features

Dual independent detector amplifiers standard

Cost

Gas Chromatograph Model 274030-00 $5140

Remarks

Optional flame photometric detector (FPD) for simultaneous operation with FID ($4100 additional)

Address

Varian Aerograph
2700 Mitchell Drive
Walnut Creek, California 94598
(415) 939-2400 TWX 910-373-1731

Physical Parameters
PHY

C. TABLE OF CONTENTS

FOR

pH, ALKALINITY, ACIDITY

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A. INTRODUCTION

The acidity or alkalinity of a water sample is defined as the amount of base or acid necessary to neutralize that sample. The hydrogen ion concentration (pH), on the other hand, is a measure of the acid or basic strength of a sample. A pH determination provides different information than does an acidity determination because of the tendency of certain substances in solution to act as buffers (a buffered solution requires the addition of a larger amount of base to cause a given change in pH than does a non buffered solution). Hence pH is a measure of the tendency of water to cause corrosion or be toxic to aquatic life while acidity or alkalinity is a measure of the amount of chemical that must be used to nullify these undesirable effects. Since the determination of acidity or alkalinity consists of a pH measurement as the sample reacts with a neutralizing agent, pH determinations will be primarily discussed. The specific types of pH measurement required to obtain values of acidity or alkalinity will be described in Section B.

1. Historical Development of pH Concept

In an effort to understand various changes that result when chemical compounds are mixed with water, Arrhenius postulated the theory of electrolytic dissociation (the ionic theory) in 1883 (Ref. 1). An important accomplishment of this theory was the identification of "acidity" with the presence of hydrogen ions (H^+), and the identification of "basicity" with the presence of hydroxyl ions. (OH^-). It was further realized that the greater the concentration of hydrogen ions released by the acid in water, the stronger the acid.

In 1909 Sorensen (Ref. 2) introduced a concept that allowed a more quantitative measure of both acid and base strength. This resulted from the realization that in aqueous solution the hydrogen ion concentration and hydroxyl ion concentration are interdependent as expressed by the relationship

$$[H^+]\,[OH^-] = 10^{-14}$$

where the square brackets indicate concentration in moles per liter. Because of this interdependence only a single parameter, either $[H^+]$ or $[OH^-]$ need be specified to define the acid strength or the basic strength of a solution. Sorensen chose $[H^+]$; and, to avoid the awkwardness of talking in terms of negative exponents, he defined the relationship

$$pH = \log\,(1/[H^+]).$$

This results in the relationships listed in Table A-1 under ideal conditions. Several characteristics of the pH unit are apparent from this table: pH of 7 corresponds to a neutral solution, the transition from a condition of a high acid to high basic strength is expressed on a scale of 0 to 14 with the meaning that low numbers characterize high acid and high numbers high basic strength, and a change of one pH unit corresponds to a 10-fold change in hydrogen ion concentration. The use of pH notation is restricted to the range from 0 to 14. If the concept were extended to more concentrated acid solutions, negative pH values would result.

TABLE A-1. Relation between ion concentrations and pH at 25°C.

pH	$[H^+]$	$[OH^-]$
0	1	10^{-14}
1	10^{-1}	10^{-13}
2	10^{-2}	10^{-12}
4	10^{-4}	10^{-10}
6	10^{-6}	10^{-8}
7	10^{-7}	10^{-7}
8	10^{-8}	10^{-6}
10	10^{-10}	10^{-4}
12	10^{-12}	10^{-2}
14	10^{-14}	1

Most determinations of pH are based ultimately on electromotive force (E.M.F.) measurements using cells composed of hydrogen electodes and a reference electrode. When such determinations are made, it is found that the relationship $pH = -\log[H^+]$ is only approximately correct. For example, a plot of the ratio of the ion concentrations as determined by EMF measurements to the concentrations known from the amount of HCl added to aqueous solutions is displayed in Fig. 1 (Ref. 3). We see from this figure that the solution behaves

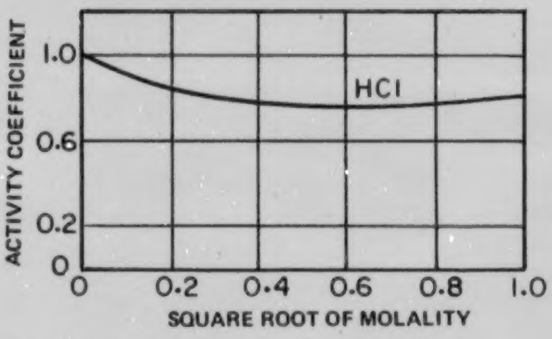

Fig. 1. Plot of activity coefficient of HCl.

as though fewer H ions and Cl ions are present than are known to correspond to the amount of HCl that has been added. Thus the HCl is not as "active" as was expected. The ratios of the measured ion concentration to the added ion concentration is referred to as the activity coefficient (Ref. 4). All acids, bases and salts in aqueous solutions display this propensity of being less active than expected except at very dilute solutions. The explanation for this lowering of activity is that there are strong electrical forces operating between ions which decrease their effectiveness (Ref. 5). This explanation is supported by pH measurements made in concentrated salt solutions (Ref. 6) (see Fig. 2).

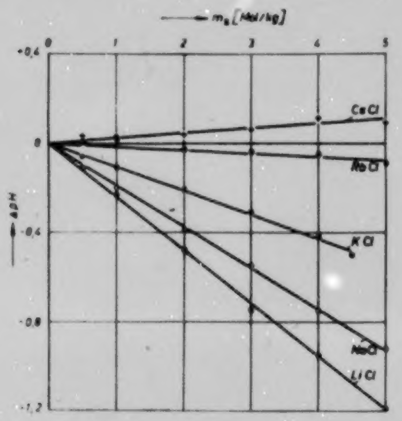

Fig. 2. pH shift of 0.01 M HCl caused by addition of LiCl, NaCl, KCl, RbCl and CsCl. (Ref.6)

From the above discussion we see that pH is not a very precisely defined term (there is a difference between the hydrogen ions added and those measured). The wide diversity of pH measurements finally awakened the realization that only a small fraction of these measurements should or could be given any interpretation involving a detailed understanding in terms of ions in solution (Ref. 7). pH measurements are obtained by placing electrodes in a variety of media, for example, in highly polluted discharges from industrial plants, in milk fluids that are undergoing conversion to cheese, in whole blood and even in soft solids such as soil that is being investigated as an ingredient in plant growth. Clearly there is little hope of interpreting such diverse measurements in terms of solution theory. However, the number that results still represents a reproducible measure of the acid strength of the medium and thus satisfies an important analytical need.

It is still possible, of course, to interpret pH measurements made in suitably constituted solutions in terms of corrected hydrogen ion concentrations. In fact, such measurements are an important tool in the application of chemical thermodynamics. But fairly strict conditions must be met for such a fundamental interpretation of pH. These conditions are discussed in texts devoted to the subject of electrochemistry (Ref. 8).

2. Practical Value of pH, Acidity, and Alkalinity Measurements

pH measurements are an important part of many industrial processes. In the chemical industry the efficient production of nylon, as well as other artificial fibers depends on rigid pH control. In the food industry the action of yeast to cause fermentation and to leaven dough is sensitive to the pH of the mix. Jellies will not jel properly unless the pH is in the region of 3.5. pH control is essential to the bleaching of wood fibers in the pulp and paper industry. Many other examples could be mentioned. However, the main concern here is the use of pH, acidity and alkalinity measurements for water quality assurance. Further remarks will be restricted to this area. Fuller treatment of the subject is contained in "Water Quality Criteria 1972" (Ref. 9).

At present water quality maintenance is primarily a function of federal, state and regional governments. This is an outgrowth of the situation when people who disagreed on proper water use took their cases to court. The basic doctrine threading through the numerous court decisions affirms the principle that no right can be acquired for a use of water that pollutes it to an extent that a downstream user suffers loss or hardship. Governmental agencies define what constitutes unreasonable pollution by establishing water quality criteria and control pollution by monitoring water quality and regulating potential abuse. pH, acidity, and alkalinity are three of the many parameters that are used to assess water quality and regulate usage.

The buffer capacity of natural waters is primarily determined by the presence of carbonates and bicharbonates. These materials are contained in natural waters because minerals are dissolved, CO_2 is absorbed from the air, and organics are decomposed as the water flows toward the sea. The concentration of bicarbonates is not only a function of the amount added but is also a function of temperature, pH, and concentration of other dissolved solids (Ref. 10,11). When a stream of water passes over carbonate containing minerals, the following reactions occur as the minerals go into solution:

$$MCO_3 + H_2O \rightarrow M^{2+} + CO_3^{2-}$$

$$H_2O + CO_3^{2-} \rightleftharpoons HCO_3^- + OH^-$$

$$H_2O + HCO_3^- \rightleftharpoons H_2CO_3 + OH^-$$

$$H_2CO_3 \rightleftharpoons CO_2 + H_2O\ .$$

If a sample of this solution is titrated with acid (alkalinity measurement), the plot of pH versus amount of acid would have the appearance of Fig. 3 (Ref. 12). The amount of acid required for the first end point (pH = 8.3) is due to the neutralization of OH^- and conversion of the CO_3^{2-} to HCO_3^-. The second end point represents the conversion of HCO_3^- to H_2CO_3. Both end points are used in the measurement of alkalinity. The first is called the caustic alkalinity and second the total alkalinity (Ref. 13).

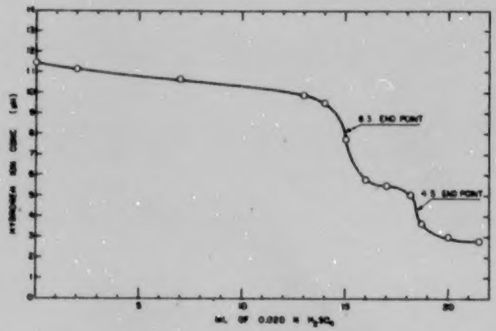

Fig. 3. Alkalinity measurement using titration with sulfuric acid endpoint. (Ref.12)

In the determination of acidity, sodium hydroxide is used to titrate to the pH 4.5 end point (mineral-acid acidity) and the 8.3 end point (total acidity) (Ref. 13). Acidity in surface or ground waters may be due to natural causes such as humic acids extracted from swamps or peat bogs or to industrial wastes (i.e., acid-mine drainage, pickling liquors, effluents from manufacturing processes, etc.).

The unit of measure of both alkalinity and acidity is mg/ℓ of $CaCO_3$. In the case of alkalinity, this unit represents the amount of $CaCO_3$ that would have been present in the water sample to react with the amount of acid used to obtain a pH of 8.3 or 4.5. In the case of acidity this represents the amount of $CaCO_3$ that would have to be added to the sample to reach the pH value of 8.3 or 4.5.

a. Water Quality for Public Water Supplies

The alkalinity of natural waters have a large range (from 20 to 500 mg/ℓ $CaCO_3$). Water that is intended for public consumption may have a wide range of alkalinity values and still be acceptable. Alkalinity below 30 to 50 mg/ℓ $CaCO_3$ should be avoided because of the danger of excessive corrosion. High alkalinity should be avoided because of a distinctly unpleasant taste and the possibility of incrustation.

Drinking waters are customarily adjusted with calcium or sodium hydroxides to reach the pH of saturation (pH_s), that is, the pH that would result if the water were saturated with calcium carbonate. The goal is usually a water which has a slight tendency to deposit calcium carbonate as a protective coating on metal surfaces. The pH_s, in bicarbonate waters, depends upon calcium concentration, concentration of other ions, temperature, and alkalinity. Low alkalinity waters have high pH_s values, sometimes 9.5 or higher, and are a special problem because of the resulting high pH values after adjustment.

Most natural waters have pH values between 5.0 and 9.0. It is recommended that water supply sources for public consumption be within this range (Ref. 9). pH values below this range may lead to corrosion that can add such constituents as iron, copper, lead, zinc or cadmium to the water system. Anticorrosion procedures currently in use make it impractical to recommend a more narrow range. It has been shown that the ability of chlorine to act as a disinfectant falls off at high pH values (Ref.14). This work indicates that it is advantageous to apply chlorine at pH values of 7 or less.

b. Quality of Recreational Waters

The pH value and the buffering capacity are important considerations of water that is intended for swimming purposes. Eye irritation results if the pH is unfavorable. The lacrimal fluid of the human eye is buffered by the presence of complex organic fluids to a pH of 7.4. When these fluids are unable to maintain the immediate eye water contact layer at this pH value, eye irritation results. A deviation of as little as 0.1 pH unit of the contact layer may cause discomfort and appreciable deviation will cause severe pain (Ref.15). Because of the high buffering capacity of the lacrimal fluid, a range of pH values from 6.5 to 8.3 can be tolerated in swimming waters. If the water has a low buffering capacity and is relatively free of dissolved solids, pH values from 5.0 to 9.0 are acceptable to most swimmers.

c. Water Quality to Preserve Aquatic Life

The effects of pH on aquatic life have been reviewed in two excellent reports (Ref. 16, 17). Summaries of these reviews are given in Table A-2 (Ref. 9). In addition to the detrimental effects caused by extremes in pH, indirect effects on aquatic life must be considered. According to the carbonate, bicarbonate equilibrium described earlier, acidification of water may release CO_2 that exerts a toxic action. (The generalizations contained in Table A-2 are only valid if the carbon dioxide level is less than 25 mg/ℓ). Another indirect effect of pH is the toxicity of metallocyanide complexes (Ref.18). A change of pH from 8.0 to 6.5 increases the toxicity of nickel cyanide a thousandfold.

In addition to providing buffering action, the carbonate system also forms a reservoir of carbon for photosynthesis. Hence the productivity of waters is closely correlated to the carbonate buffering capacity, the biological productivity being reduced in proportion to the degree of reduction of buffering capacity. Because of this correlation, it is recommended that alkalinity of natural waters not be decreased more than 25% below the natural level. In addition, for maximum protection of aquatic life, pH should be in the range 6.5-8.5 (Ref.9).

d. Quality of Water for Agricultural Use

The pH value of irrigation waters has little direct effect on the agricultural usefulness. This results because soil is a strongly buffered system relative to the buffering strength of most irrigation waters. There are, however, limits. For example, water of pH less than 4.8, if used for an extended period of time, will result in the formation of soluble iron, aluminum or manganese salts that can be toxic to plant growth. Waters in which the pH value exceeds 8.3 contain high concentrations of sodium carbonates and bicarbonates which can also be toxic to plant growth. Waters with pH values in the range 4.5 to 9.0 should be usable for irrigation; however, care should be taken to detect the development of harmful indirect effects.

e. Quality of Estuarine Water

In the marine environment imports and exports continually occur from coastal runoff, tidal action, ocean currents, exchanges with adjacent water bodies and interaction with the atmosphere. The estuaries are in many ways the most complicated and variable of aquatic ecosystems. Materials carried from the land by rivers vary in quantity and quality and show strong seasonal patterns. Tidal oscillations cause vigorous reversals of flow. Dense urban populations on the shores produce large amounts of waste and engineering projects may change boundaries and flows of water courses.

Estuaries are very important in the support of fisheries; at least three quarters of the species in the commercial and recreational fisheries of the nation are dependent upon the estuarine ecosystem at one or more stages of

TABLE A-2. A summary of some effects of pH on fresh-water fish and other aquatic organisms.

pH	Known effects	Ref.9
11.0-11.5	Rapidly lethal to all species of fish.	
10.0-10.5	Withstood by salmonids for short periods but eventually lethal. Exceeds tolerance of bluegills (Lepomis macrochirus) and probably goldfish. Some typical stoneflies and mayflies (Ephemera) survive with reduced emergence.	
9.0-9.5	Likely to be harmful to salmonids and perch (Perca) if present for a considerable length of time and no viable fishery for coldwater species. Reduced populations of warmwater fish. Carp avoid these levels.	
7.0-8.0	Full fish production. No known harmful effects on adult or immature fish, but 7.0 is near low limit for Gammarus reproduction and perhaps for some other crustaceans.	
6.5-7.0	Not lethal to fish unless heavy metals or cyanides that are more toxic at low pH are present.	
6.0-6.5	Unlikely to be toxic to fish unless free carbon dioxide is present in excess of 100 ppm.	
5.0-5.5	Very restricted fish populations but not lethal to any fish species unless CO_2 is high (over 25 ppm), or water contains iron salts.	
4.0-4.5	Fish populations limited; only a few species survive. Perch, some coarse fish, and pike can acclimate to this pH, but only pike produce. Lethal to fathead minnow. Some caddis flies and dragonflies found in such habitats; certain midges dominant. Flora restricted.	
3.0-3.5	Unlikely that any fish can survive for more than a few hours. A few kinds of invertebrates such as certain midges and alderflies, and a few species of algae may be found at this pH range and lower.	

their life history (Ref. 9). Estuaries are used as spawning grounds, nursery areas, havens from parasites and predators and as rich sources of food. However, there are characteristics of these bodies of water that tend to reduce the effects of man's activities.

The buffer capacity of sea water is much greater than fresh water because of the presence of large amounts of salts. This buffering capacity diminishes the harmful effects of highly acidic or alkaline wastes compared to the fresh water situation. The CO_2-HCO_3^--CO_3^{2-} equilibrium is described in detail in texts dealing with the chemistry of the oceans (Ref. 19,20).

The variation of pH with depth is illustrated in Fig. 4 (Ref.21). These variations are largely explained in terms of the effect of variation of CO_2 concentrations on the carbonate equilibrium. At the surface the CO_2 concentration is determined by the partial pressure in the atmosphere, the temperature and the salinity. Release of CO_2 because of biological activity (decomposition and respiration) is responsible for the pH decrease to the depth of about 200 meters. (Most estuarine waters are less than 200 meters deep). Below this depth the lack of available O_2 prevents the generation of more CO_2 so the pH begins to rise. The maximum found at the 3500 meter level is believed to be due to pressure effects on the carbonate equilibrium. In estuarine waters, particularly in warm tropical and subtropical areas, there is a large diurnal variation in pH with values ranging from a high of 9.5 during the day to a low of 7.3 at night (Ref.9).

Plankton and benthic invertebrates, the important food sources of the oceans, are probably more sensitive to changes in pH than are higher life forms. Oyster performance (rate of pumping) decreases as the pH changes from 7.0 to 6.5. Oyster larvae are impaired at pH 9.0 (Ref. 22). The upper pH limit for crabs is 10.2 (Ref.23). Changes in sea water pH should be avoided in order to minimize environmental impact. The normal range of pH in either direction should not be extended by more than 0.2 units. Addition of foreign material should not drop the pH below 6.5 or raise it above 8.5 (Ref. 9.)

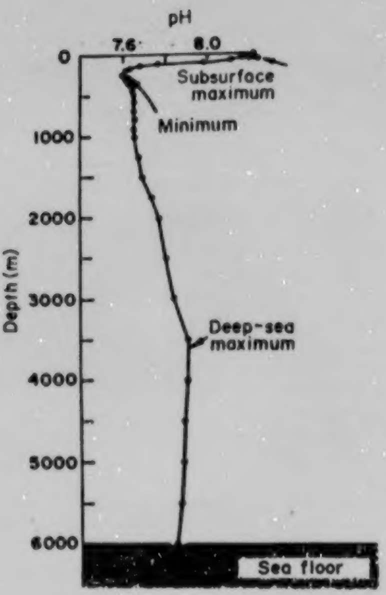

Fig. 4. Variation of pH with depth in sea water. (Ref.21)

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B. MEASUREMENT METHODS FOR pH, ALKALINITY, AND ACIDITY

In order to determine any of the three parameters, pH, alkalinity, or acidity, a measurement of some quantity that is related to the hydrogen ion concentration must be made. In the determination of alkalinity (or acidity) the capacity of a water sample to take up (or donate) hydrogen ions is measured by finding the amount of acid (or base) needed to bring the sample to a specific pH. The pH is determined either by measurement of the electrochemical potential that exists between different solutions or by the color of certain organic compounds that are sensitive to the presence of hydrogen ions. The electrochemical method is, by far, the most common method because of the ease of performing the measurement and the broad area of application (pH of liquids of a wide range of viscosities as well as soft solids can readily be measured). The indicator method is highly unreliable unless used by an expert in research circumstances. The advent of the transistor and integrated circuits has greatly reduced the cost and increased the convenience of the electrochemical method.

1. Electrochemical Methods

In order to determine pH by electrochemical methods, a system must be devised for comparing the driving force of the reaction

$$2H^+ + 2e^- = H_2$$

with the driving force of some other reaction. (This type of comparison is a measure of the relative reactivity of various chemical systems.) It is known from experiment that the driving force of this reaction depends on the hydrogen ion concentration; hence this can be used as a measure of pH.

The comparison of the driving force of two chemical reactions is accomplished by measuring the voltage developed between metallic probes that are in contact with the two different reaction media. The reaction media metallic probe combination is defined as an electrode. A way must be found of allowing electrons to flow from one electrode to the other without the solutions intermixing. Finally, the two electrodes must be connected to a potentiometer to measure the EMF (electromotive force) that exists between the two chemical systems. One way of providing an electron path without danger of solution mixing is illustrated in Fig. 1 (Ref. 1). A common reference electrode is the mercury-mercurous chloride (saturated calomel) system for which the electrode reaction is

$$Hg_2Cl_2 + 2e^- = 2Hg + 2Cl^-.$$

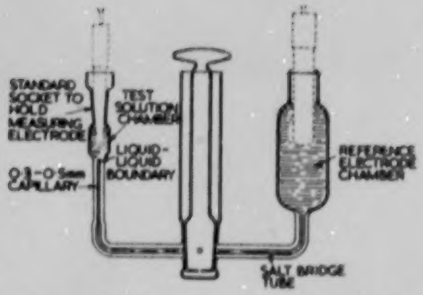

Fig. 1. Use of salt bridge to provide electron path between test solution and reference electrode. (Ref. 1).

Present day commercially available electrodes contain all the ingredients that are required to make the above described comparisons in a small compact package. To make a pH measurement the two electrodes are placed in the test solution and the pH value is displayed on a meter. The design details of these combination electrodes will be described later.

The influence of hydrogen ion concentration on the EMF measured in a cell of this type is given by the equation

$$E = E^0 - 0.1984\ T \log a(H^+)a(Cl^-)$$

where $a(H^+)$ and $a(Cl^-)$ represent the activity of the H^+ and Cl^- (roughly the same as the concentration of these ions in moles/liter).

T = absolute temperature

E^0 = the EMF (in millivolts) that would be obtained if $a(H^+) = a(Cl^-) = 1$ and $T = 25°C$

and

E is in millivolts.

Since $a(Cl^-)$ is constant in the reference electrode, the EMF of the cell is a measure of the pH if T is kept constant.

The widespread use of pH measurements for industrial and clinical purposes led to the realization that only a small fraction of these measurements could, or should, be given any interpretation in terms of solution theory (Ref. 2). Instead, a definition in terms of operational procedure was needed. The following definition has been endorsed by standardizing groups in the United States (Ref. 3) and in Great Britain (Ref. 4) and has been the subject of reports to the International Union of Pure and Applied Chemistry.

$$pH = pH_s + \frac{E - E_s}{2.3026\ RT/F}$$

where E = the measured EMF of the sample
E_s = the measured EMF of a standard buffered soltuion

pH_s = the pH of the standard buffered solution
R = 8.316 volt coulombs/degree
T = absolute temperature
and
F = 93,490 coulombs (the Faraday).

The National Bureau of Standards has assigned pH values to four primary standards and two secondary standards (Ref. 5). Using this definition greatly simplifies interlaboratory comparison of complex chemical solutions (e.g., blood, urine, plant effluents). It is only necessary to measure the EMF of the sample, the EMF of the standard solution and perform a simple calculation.

A variety of different sensing electrodes and reference electrodes may be used for pH measurements. The ultimate standard for the sensing electrode is the hydrogen gas electrode; one form of which is pictured in Fig. 2 (Ref.6). This electrode consists of a small platinum sheet, coated with platinum black, that is suspended in the test solution through which is passed a stream of hydrogen at atmospheric pressure (platinum black is a coating that results when platinum is electroplated such that there is a large surface area). The position of the electrode is arranged so that it is partly in solution and partly in the atmosphere of hydrogen gas. For a more detailed description of hydrogen electrodes and reference electrodes the reader should consult a standard text on electrochemistry (e.g., Refs. 5 and 6). The remainder of this discussion will be concerned with the use of the glass electrode for pH measurements because of its wide use for industrial and environmental applications.

A glass electrode that is responsive to pH is pictured in Fig. 3 (Ref. 7). The chemical and physical processes that explain the response of this electrode are not well understood. There is no reason to believe that hydrogen ions actually pass through the glass. A more likely explanation is that a hydrated gel layer forms on both the inner and outer surface of the pH responsive glass. The absorption of hydrogen ions by an ion exchange type process sets up an electrical charge that is sensed by the hydrated gel on the other side. It is the change of this potential as the hydrogen ion concentration changes that is responsible for the change in measured EMF. The lifetime of the electrode is determined by the dissolution rate of these hydrated gel layers. The lifetimes vary from a few weeks to several years depending on the type of glass used and the type of measurements made with this electrode (Ref. 7). Harsh chemical environments that corrode the glass membrane will shorten the life.

A piece of bare wire dipped into the test solution could be used as the reference electrode. But, if this were done the voltage at its surface would change with time because of corrosion and would vary depending upon the nature of the test solution. In order to avoid these problems, a reference electrode of the type depicted in Fig. 4 is used (Ref. 8). This

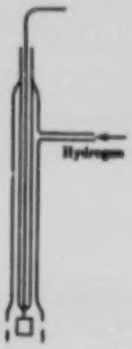

Fig. 2. One type of hydrogen gas electrode. (Ref. 6).

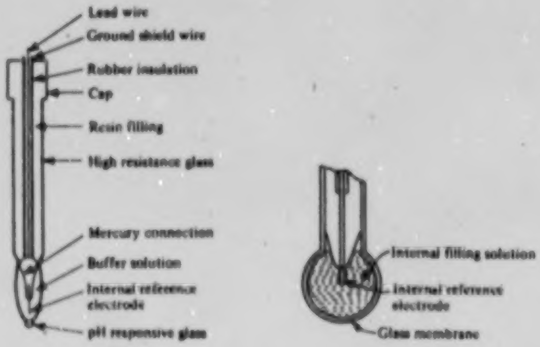
Lead wire
Ground shield wire
Rubber insulation
Cap
Resin filling
High resistance glass
Mercury connection
Buffer solution
Internal reference electrode
pH responsive glass
Internal filling solution
Internal reference electrode
Glass membrane

Fig. 3. Construction of glass membrane, pH-responsive electrode. (Ref. 7).

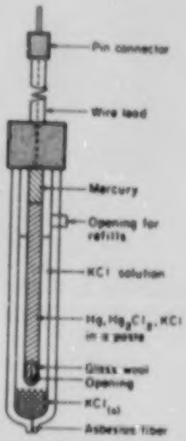
Pin connector
Wire lead
Mercury
Opening for refills
KCl solution
Hg, Hg2Cl2, KCl in a paste
Glass wool
Opening
KCl(s)
Asbestos fiber

Fig. 4. Combination mercury-mercurous chloride electrode and salt bridge. (Ref. 8).

commercial electrode combines a salt bridge of the type in Fig. 1 and a mercury-mercurous chloride reference electrode in the same package. An example of a commercial electrode that combines the glass electrode, connecting bridge, and reference electrode in the same package is depicted in Fig. 5 (Ref. 9). Technological response to the need for many specific types of electrodes has resulted in a wide variety of models, shapes and sizes now being commercially available.

When the glass electrode behaves in an ideal fashion (responding to change in pH the same way as does the hydrogen electrode), the voltage change corresponding to a change of 1 pH unit is 59.16 mV at 25°C (Ref. 10). Most glass electrodes have an ideal response from pH of 0 to pH 12. Some electrodes display voltage departures above pH 11 in solutions of high salt concentration, especially at temperatures above room temperature. Errors of this type for some commercially available electrodes have been tabulated (Ref. 11). When not in use, glass electrodes should be stored in water. A dry electrode may require several hours conditioning (time required before a constant voltage reading is obtained). The operation of the electrode is suspect if the glass membrane becomes cracked or scratched.

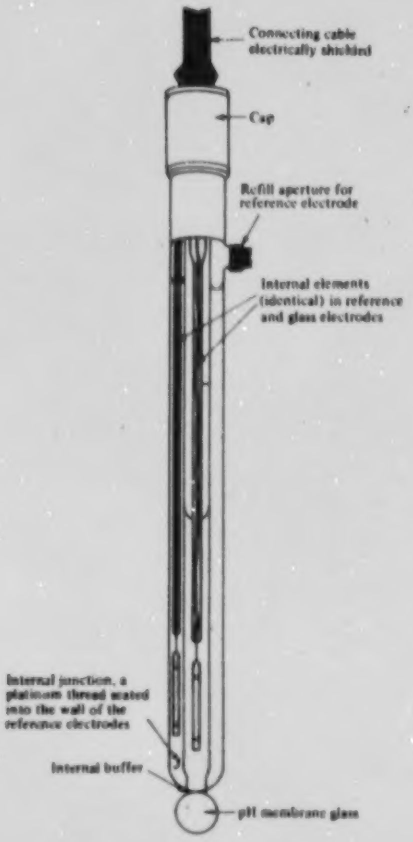
Connecting cable electrically shielded
Cap
Refill aperture for reference electrode
Internal elements (identical) in reference and glass electrodes
Internal junction, a platinum thread seated into the wall of the reference electrodes
Internal buffer
pH membrane glass

Fig. 5. A combination ph-bridge-reference electrode distributed by Sargent Welch Company. (Ref. 9).

2. Color Indicators

An indicator is any substance that relates the progress of a chemical reaction by a visual presentation. More specifically, for acid-base reactions, an indicator is a substance that undergoes a visible change over a fairly narrow pH interval. Although a number of visible changes have been used (e.g., turbidity arising from precipitation or flocculation of a colloid, onset or disappearance of fluorescence) by far the most common type of indicator relies on a change in color. The indicators are organic dyes that behave as weak acids or weak bases. The color results because certain functional groups of the dye absorb light of a part of the visible spectral region. A change of the pH causes a change in the composition of the functional groups with a resultant change in the spectral region over which light is absorbed. An illustration of the processes that occur when phenolphthalein is used as an indicator is contained in Fig. 6 (Ref. 12). The acidic (colorless) form of this indicator exists at pH less than 8.4 and is shown on the left and the basic (red) form (pH > 10.0) is shown on the right.

The description of the color changes that occur as the pH is changed suggest that the transition from the acidic form to the basic form is not sharp. Rather, the two forms exist in equilibrium such that the relative concentrations change as the pH changes. The transformation is regarded as complete when the color of the first form can no longer be detected in the presence of the second form. The width of the interval over which the two forms coexist varies depending upon the indicator. Table I (Ref. 13) lists some useful indicators along with the pH range over which the two forms coexist. Paper impregnated with these indicators (pH paper) is used for crude pH determinations.

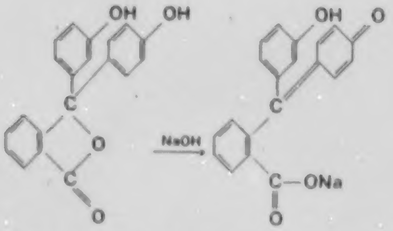

Fig. 6. Change in functional groups that occur in phenolphthalein as the pH is changed from 8.4 to 10.0. (Ref. 12).

TABLE B-1. Some useful indicators and their color change characteristics.(Ref.13)

Trade name	pH Range	Color change, acid-alkaline
o-Cresol red (acid range)	0.2-1.8	Red-yellow
Thymol blue (acid range)	1.2-2.8	Red-yellow
Pentamethoxy red	1.2-3.2	Red-violet-colorless
Tropeolin 00	1.3-3.2	Red-yellow
2,4-Dinitrophenol	2.4-4.0	Colorless-yellow
Methyl yellow	2.9-4.0	Red-yellow
Methyl orange	3.1-4.4	Red-orange
Bromophenol blue	3.0-4.6	Yellow-blue-violet
Tetrabromophenol	3.0-4.6	Yellow-blue
Alizarin sodium sulfonate	3.7-5.2	Yellow-violet
α-Naphthyl red	3.7-5.0	Red-yellow
p-Ethoxy chrysoidine	3.5-5.5	Red-yellow
Bromoersol green	4.0-5.6	Yellow-blue
Methyl red	4.4-6.2	Red-yellow
Bromocresol purple	5.2-6.8	Yellow-purple
Chlorophenol red	5.4-6.8	Yellow-red
Bromothymol blue	6.2-7.6	Yellow-blue
p-Nitrophenol	5.0-7.0	Colorless-yellow
Azolitmin	5.0-8.0	Red-blue
Phenol red	6.4-8.0	Yellow-red
Neutral red	6.8-8.0	Red-yellow
Rosolic acid	6.8-8.0	Yellow-red
Cresol red (alk.range)	7.2-8.8	Yellow-red
α-Naphtholphthalein	7.3-8.7	Rose-green
Tropeolin 000	7.6-8.9	Yellow-rose-red
Thymol blue (alk.range)	8.0-9.6	Yellow-blue
Phenolphthalein	8.0-10.0	Colorless-red

In the determination of the alkalinity of water samples the test solution is titrated to a specific pH with a strong mineral acid. Generally the basic nature of the sample is due to the carbon dioxide-bicarbonate-carbonate equilibrium. Titration to the phenolphtalein end point (pH = 8) is a measure of the amount of carbonate in the sample (Ref. 14). Titration to the pH range 4 - 5 is a measure of the total alkalinity of the sample. Methyl orange indicator is recommended for the total alkalinity determination. Both the phenolphtalein alkalinity and the total alkalinity are used for calculating the dosages required in the treatment of natural water supplies. Acidity is also determined by titrating to a methyl orange and phenolphthalein end point (Ref. 14).

A number of difficulties are involved in pH measurements through the use of indicators. Neutral salts may affect the light absorbing properties, the indicator may react with various substances in the test solution (e.g., detergents, proteins) turbid or colored solutions make the indicator color difficult if not impossible to perceive and the indicator color tone is dependent on the temperature of the solution. These factors combine to make indicator pH measurements, as usually performed, more uncertain than electrometric pH measurements.

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C. INSTRUMENTATION FOR pH MEASUREMENTS

In order to measure the pH of any test solution by electrochemical methods it is necessary to measure the EMF that exists between the indicator electrode (electrode that is sensitive to hydrogen ion concentration) and the reference electrode (electrode that is not affected by the hydrogen ion concentration). A simple voltmeter cannot be used for this measurement since if current flows during the measurement an error will be introduced. This can be seen from the following example.

Assume the voltage between the indicator and reference electrode is 1.0 V and the cell resistance is 100 MΩ. If the resistance in the voltage measuring device is 1,000 MΩ, the flowing current is

$$i = \frac{E}{R} = \frac{1.0}{10^8 + 10^9} = 9.0 \times 10^{-10} \text{ A.}$$

As this current flows between the electrodes it overcomes the cell resistance generating a voltage that opposes the cell voltage. This opposing voltage is equal to

$$i R_{cell} = (9\times10^{-10})\ (1\times10^8) = 0.09 \text{ V.}$$

Hence the measured cell voltage is only 0.91 V or an error of 9% has been introduced. Since the resistance of glass electrodes ranges between 5 and 500 MΩ, this is a fairly realistic example.

In order to minimize the flow of current during pH measurement a circuit of the type pictured in Fig. 1 is used (Ref. 1). When the glass and reference electrodes are not immersed in a test solution they are electrically isolated from each other. The circuit is designed so that under this condition a null indication is displayed on the meter. When the electrodes are inserted into the test solution, an EMF appears on the grid of the triode (the triode acts as a signal amplifier in this system). The grid EMF is varied by changing the value of the resistance, R, until a null indication is again obtained. The position of R has previously been calibrated in millivolts or pH units. Current flow through the cell during the measurement is minimized by utilizing a null indication technique with a triode amplifier. Since the resistance of the glass electorde is so high (~ 10^8 Ω), in order to achieve an accuracy of 0.1% the resistance (impedance) of the amplifier must be greater than 10^{11}Ω. When tube type amplifiers were used, this could only be achieved with selected vacuum tubes. The development of field-effect transistors (FETs) has led to the development of amplifiers with imput impedance of 10^{12}Ω or more (Ref. 2). An excellent description of the mechanism of FET operation along with a discussion of applications to analytical chemistry is contained in the text "Instrumental Methods of Analysis", by Willard Merrit and Dean (Ref. 3).

A more convenient method of pH measurement would result if the circuit in Fig. 1 were designed so that the meter display directly related to the pH of the cell and the adjustment for null indication could be omitted. This means that the measurement would be made with current flowing through the cell. The advent of solid state electronics (especially FETs) has made possible the amplification of such small currents that this is now the method of operation of most commercial pH meters.

Commercially available pH meters range in price from less than $100 to more than $1000. In addition to pH measurement, most meters are designed to be used in oxidation reduction potential (ORP) measurement and some meters are designed to be used with specific ion electrodes. The features that determine the price are many. Examples are accuracy, automatic temperature correction, Nernst correction (required when working over large enough pH range that the relation to hydrogen ion concentration is not linear), and digital read out.

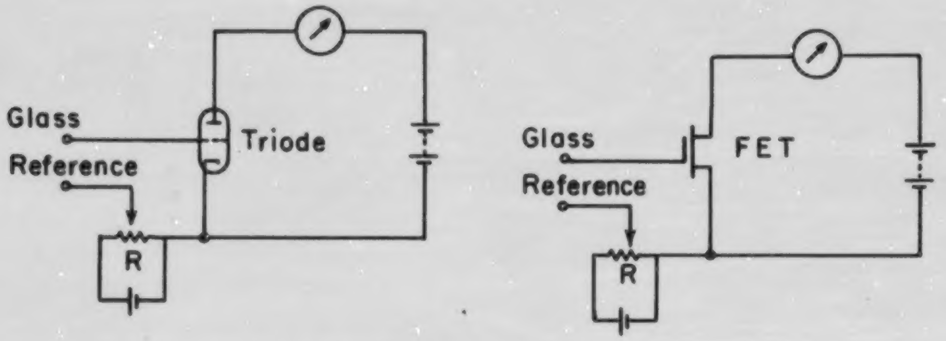

Fig. 1. Principle of pH meter amplifiers.

and adjusting a standarize knob until the meter reading agrees with the known value. The electrodes are removed, rinsed, wiped and then placed in the unknown solution. The pH of the unknown can then be read off the meter. When less expensive instruments are used, slow drift will occur and the instrument must be standardized often. If the value of the unknown solution differs by more than one pH unit from the standard, a new standard that is closer to the value of the unknown may be used to recalibrate. The closer the standard value to the unknown, the more accurate the reading.

In addition to the pH indications most meters also are calibrated in millivolts(mV). These readings are used for determination of the endpoint of an acid base titration, an oxidation reduction reaction or with specific ion electrodes. The millivolt range over which this instrument operates varies from ± 300 mV to ± 2000 mV, the larger range being available in the more expensive instrument. For use with specific ion electrodes good sensitivity is required. This is true because a change of 1 pH unit corresponds to 60 mV (at 25°C) whereas a change of concentration of a specific ion by one unit may correspond to only a 3 or 4 mV change.

The mV change corresponding to a given change in ion concentration has the temperature dependence described by the Nernst equation. The common way to correct for this dependence is to measure the temperature of the solution whose pH is to be determined and position a dial at that temperature reading. This has the effect of changing the gain of the instrument so that a change of 1 unit on the pH scale corresponds to the following number of millivolts:

0°C	54 mV
25°C	60 mV
50°C	64 mV
75°C	68 mV
100°C	70 mV.

It is possible to purchase with some meters an automatic temperature control (ATC). This is a temperature sensing device (i.e., thermocouple) that is placed in the test solution along with the pH electrodes. The signal from this device automatically adjusts the gain to compensate for the temperature. It is also possible to purchase instruments that allow the temperature to be displayed on a digital meter if a switch is placed in the proper position. The temperature correction is then made by turning a dial to correspond to the digital display.

Another correction device that is included with some pH meters is the Nernst corrector. This feature allows the instrument to be standardized against solutions of two different known values of pH. Values are chosen that bracket those expected from the measurement of a series of unknowns. The meter is adjusted to give the correct value of one solution using the standarize dial. It is then adjusted to give the correct value of the second solution using the Nernst corrector (slope corrector) dial. pH readings between these values are somewhat more accurate than would be obtained with a meter that could only be standarized to one value.

In addition to features that affect accuracy such as the temperature corrector and Nernst corrector, instrument stability and electrode compatability should also be considered. The stability is especially important if it is desired to connect the instrument to a chart recorder for a continuous output. The most common electrode arrangement uses a major jack on the pH measuring electrode and a "phone-tip" jack on the reference electrode. A variety of BNC or twist-type connectors, "banana jacks" and various size male connectors are used. Since electronic pick-up is a problem, the electrode leads must be carefully shielded. Therefore, care is required if an attempt is made to adapt a connector. For these reasons an effort should be made to determine the source of compatible electrodes before instrument purchase.

Electrodes are included in the purchase price of most instruments that are listed in the table (Section E). An effort was made to indicate those cases where this was not true. pH instruments that were designed for special purposes (i.e. pH control units) are not included in this table. A number of accessories are available with some instruments. These include such things as extension cables to electrodes, weather proof housing, recorder output with adjustable gain, switch selection for battery or AC operation and special switches that allow malfunction to be traced to the electrodes or the instrument. The presence of the temperature corrector and Nernst corrector has been indicated in the table but accessories have not. A separate row was used to describe the expanded scale characteristics of instruments that have this feature. An attempt was made to include only manufacturers and exclude distributers. This was somewhat difficult since some distributers affix their company name to instruments manufactured by someone else.

The potential buyer should be cautious of the terms accuracy, reproducibility and readability. The accuracy of the instrument depends on the ability of the instrument to measure operationally useful pH values that depart from the pH at which the instrument was standardized. This can only be determined by the use of multiple standardizations with buffers covering the range of interest. Unless accuracy values are stated in terms that define the difference of the sample pH and the standardization pH, they have no useful meaning. The reproducibility depends upon the time that has elapsed between the taking of the initial reading and the attempt to reproduce that reading. If this time interval is not specified the value has little meaning. The readability depends upon the ability to estimate the position of a pointer between two marks and varies from observer to observer.

A grouping of instrumentation into the categories utility, general purpose, expanded scale and research has recently been carried out by Hauber and Dayton (Ref. 4). These categories include meters that are accurate to 0.1, 0.05, 0.01 and 0.001 pH unit respectively, 98 models produced by 24 manufacturers are included in this survey. Two other surveys have appeared in the last few years. One groups the instruments into pH meters and specific ion meters (Ref. 5). The other is mainly concerned with the characteristics of European instruments (Ref. 6). The information presented in the present survey was obtained by contacting manufactures listed in three different guides to scientific instrumentation (Ref. 7,8,9). No attempt was made to group instrumentation into categories other than that the instruments produced by the same manufacturer appear together.

The potential buyer should make his own grouping depending upon the money available and the accuracy (reproducibility) required. Some consideration should also be given to ease of operation and instrument maintenance. These factors can best be evaluated by talking to people who have already purchased pH meters.

Instrumental pH measurements are almost always made by first standardizing the meter against a solution of known pH. This is done by placing the electrodes in a known pH solution

Of course the price of instruments varies in a way that reflects the effects of inflation upon the economy which means that the cost indicated in the table may not be accurate in a few years. However these figures will still be valuable to indicate relative cost of different instrument models.

D. ACKNOWLEDGMENT

The helpful criticisms and suggestions of Joseph J. Connors, Water Quality Supervisor, East Bay Municipal Utility District, and George A. Morton, Consultant, Lawrence Berkeley Laboratory, are gratefully acknowledged.

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E. TABLE OF COMMERCIALLY AVAILABLE pH INSTRUMENTS

	Model	cost	pH range	mv range	recorder output	accuracy	reproducibility	smallest scale division	power	readout	temperature compensated	remarks
Amstro Corporation												
	PH-IT	255	1-13			0.1pH		0.2pH	Bat	meter	10-80°C	
	PH-2A	370	0-14	0-1400	yes	0.05pH 5mv		0.1pH 10mv	AC	meter	0-100°C	Bat option
	expanded scale operation			-140 to +140		1mv		2mv				
	PH-3T	245	1-13			±0.1pH			Bat	meter	10-80°C	
	PH-4	515	0-8 6-14	-200 to +1400 +200 to -1400	yes	0.025pH 5mv		0.05pH 10mv	AC	meter	0-100°C	
	expanded scale operation		3.5-7.5 6.5-10.5	-20 to +140 +20 to -140		0.025pH 0.5mv						
Analytical Measurements												
	30 AC	430	2-12		recorder included			0.2pH	AC	meter recorder	0-100°C	ATC option
	30 DC	475	2-12		recorder included			0.2pH	Bat or AC	meter recorder	0-100°C	

Model	cost	pH range	mv range	recorder output	accuracy	reproducibility	smallest scale division	power	readout	temperature compensated	remarks
Analytical Measurements (cont.)											
107	125	2-12						Bat	meter		
707	145	0-14			±0.1pH		0.1pH	AC			
707-B	145	0-14							meter	0-100°C	
721	345			yes	0.01pH						
Aquatronics											
120	395	0-14			±2% of full scale			AC	meter	0-100°C auto manual	Bat option Field use
110	1195	1-13		recorder included				Bat	chart	0-100°C auto	AC option Field use
Beckman Instruments, Inc.											
3500	580	0-14	+1999 to -1999	yes	±0.01pH	±1mv	0.01pH	AC	digital	0-100°C manual	Nernst corrector
3550	725	0-14	+1999 to -1999	yes	±0.01pH	±1mv	0.01pH	AC	digital	0-100°C manual	Nernst corrector also reads temperature

	Model	cost	pH range	mv range	recorder output	accuracy	reproducibility	smallest scale division	power	readout	temperature compensated	remarks
eckman (cont.)	Instruments, Inc. 4500	950		+1999.9 to -1999.9	yes	±0.001pH	±0.1mv	0.001pH	AC	digital	0-100°C manual	Nernst corrector
	Chem-Mate	215	0-14	+700 to -700		±0.1pH ±10mv		0.1pH 10mv	Bat AC	meter	0-100°C manual	
	Ex-pand-mate {expanded scale operation	265	0-14			±0.02pH		0.01pH	Bat AC			non-expanded scale operation same as Chem-Mate
	Century SS-1	870	0-14	+1400 to -1400	yes	±0.05pH		0.1pH	AC	meter	0-100°C manual	ATC option Nernst corrector
	expanded scale operation					±0.007pH		0.0pH 1mv				
	Expandomatic SS-2	695	0-14	+1400 to -1400	yes	±0.05pH		0.1pH	AC	meter	0-100°C manual	ATC option
	expanded scale operation					±0.01pH		0.01pH 1mv				
	Zeromatic SS-3	495	0-14	± 700 ±1400	yes	±0.05pH	±0.015pH	0.1pH 10mv	AC	meter	0-100°C manual	
	Electromate	460	0-14	± 700	yes	±0.08pH ±10mv	0.02pH 2mv	0.1pH 10mv	AC Bat	meter	0-100°C manual	

Model	cost	pH range	mv range	recorder output	accuracy	reproducibility	smallest scale division	power	readout	temperature compensated	remarks
Beckman Instruments, Inc. (cont.)											
pHistol	129	2-12				±0.1pH		Bat	meter		
pHASAR-1	535	0-14	±1999	yes	±0.01pH ±1mv		0.01pH	AC	digital liquid crystal	0-100°C manual	ATC option Nernst corrector
Belnor Systems Inc.											
pHase 1	595	0.00 to 14.00	±999.9		0.01pH			Bat AC	digital	0 to 100°C manual	
Micro 50	99	2-12			±0.1pH				meter	0 to 100°C manual	
Brinkmann Instruments, Inc.											
pH103	695	0.00 to 13.99	-1999 to +1999	yes	±0.01pH	0.01pH	0.01	AC	digital	0-100°C manual	ATC option Nernst corrector
pH102	850	0.00 to 13.99		yes	±0.01pH	0.01pH		AC	digital	0-100°C manual	ATC option Nernst corrector
expanded scale operation		0.000 to 13.999	-1399.9 to +1399.9		±0.002pH	0.001pH	0.001	AC	digital		
E512	655	0 to 14	±700	yes	0.025pH 10mv		0.1pH 10mv		meter	0-100°C manual	ATC option or Nernst corrector
expanded scale operation		±1.4	±140		0.005pH 2mv	0.005pH 0.5mv	0.02pH 2mv				

	Model	cost	pH range	mv range	recorder output	accuracy	reproducibility	smallest scale division	power	readout	temperature compensated	remarks
Cambridge Instrument Co.												
	5006		0-14	±400		±0.1pH			AC	meter	0-100°C manual	
Capco Chemical Analysis Products Co.												
	J-3A	398	0-14	±1400	yes	±0.05pH ±7mv	±0.02pH ±2mv		AC		0-100°C manual	
	expanded scale operation		any 1.4	140		±0.007pH ±1mv	±0.002pH ±0.2mv					
Chemtrix Inc.												
	40	89	0-14	±700		0.05pH		0.1pH	Bat	meter	0-100°C	electrodes not included
	40 AC	119	0-14	±700		0.05pH		0.1pH	AC	meter	0-100°C	electrodes not included
	40E { expanded scale operation	119				0.005pH		0.01pH	Bat	meter		electrodes not included
	40E-AC { expanded scale operation	144				0.005pH		0.01pH	AC	meter		electrodes not included
	60A	289	0-14	±1999	yes	0.01pH			AC	digital	0-100°C	electrodes not included

	Model	cost	pH range	mv range	recorder output	accuracy	reproducibility	smallest scale division	power	readout	temperature compensated	remarks
Chemtrix Inc. (cont.)	41/R	249	2-12		recorder included			0.2pH	AC	chart paper		electrodes not included
	41R/B	349	2-12		recorder included			0.2pH	Bat	chart paper		electrodes not included
Corning Science Products Division	3	120	2-12	±300	no	±0.2pH ±12mv	±0.1pH ±6mv	0.2pH 12 mv	Bat	meter	0-100 °C	
	5	310	0-14	±700	yes	±0.1pH ±10mv	±0.05pH ±3mv	0.1pH 10mv	AC	meter	0-100 °C	ATC option
	610A	350	0-14	±700	yes	±0.1pH ±10mv	±0.05pH ±3mv	0.1pH 10mv	Bat AC	meter	0-100 °C	ATC option
	expanded scale operation		any 1.4pH	140mv		0.01pH ±1mv	±0.05pH ±0.3mv	0.01pH 1mv				
	7	550	0-14	±1400	yes	±0.05pH ±10mv	±0.02pH ±5mv	0.1pH 10mv	AC	meter	0-100 °C	ATC option
	109	625	0-14	±1900	yes	±0.01pH ±1mv	±0.01pH ±1mv	0.01pH 1mv	AC	digital	0-100 °C	ATC option
	119	650	0-14	±1800	yes	±0.01pH ±2mv	±0.01pH ±1mv	0.01pH 1mv	AC	digital	0-100 °C	push-botton calibration ATC option

Model	cost	pH range	mv range	recorder output	accuracy	reproducibility	smallest scale division	power	readout	temperature compensated	remarks
Corning Science Products Div. (cont.) 10	695	0-14	±1400	yes	±0.05pH ±14mv	±0,02pH ±2mv	0,05pH 5mv	AC	meter	0-100°C	ATC option
expanded scale operation		any 3pH	300		±0.01pH ±3mv	±0.005pH ±0.5mv	0.01pH 1mv				
12	870	0-14	±1400	yes	±0.1pH ±7mv	±0.02pH ±2mv	0.1pH 10mv	AC	meter	0-100°C	ATC option
expanded scale operation		any 1pH	any 100mv		±0.005pH ±0.5mv	±0.002pH ±0.2mv	0.005pH 0.5mv				
110	1100	0-14	±1800	yes	±0.01pH ±1mv	±0.01pH ±1mv	0.01pH 1mv	AC	digital 4 digit	0-100°C	Nernst correction ATC option
expanded scale operation		any 1pH	±1800		±0.001pH ±0.1mv	±0.001pH ±0.1mv	0.001pH 0.1mv				
112	1250	0-14	±1800	yes	±0.001pH	±0.001pH ±0.1mv	0.001pH 0.1mv	AC	digital 5 digit	0-100°C	Nernst correction ATC option
Data Technology 14	499	0-14	±1999	yes	±0.01pH	±0.01pH ±1mv		AC	digital	0-100°C manual auto	BCD option Nerst correction
Delta Scientific 1012	149	2-12			0.15pH	0.05pH	0.1pH	Bat	meter	0-100°C	

Model	cost	pH range	mv range	recorder output	accuracy	reproducibility	smallest scale division	power	readout	temperature compensated	remarks
Delta Scientific (cont.)											
1112	298	0-14	±600	0.1pH 10mv				Bat	meter	0-100°C	Nernst correction
3312-01	1190	2-12	±500	recorder included					chart paper	0-50°C auto	
Devon Products, Inc.											
310	148	0-14			0.1pH		0.2pH	Bat	meter		
300	218	any 2 pH units			0.05pH						
100	226	0-14	±700		0.05pH		0.1pH	Bat	meter	yes	
101	249	0-14	±700					AC	meter		
140	275	0-14	±700		0.5pH		0.1pH	AC	meter	0-100°C	
expanded scale operation		2pH units	200		0.05pH		0.01pH 2mv	meter			
132	468	0-14			0.1pH			AC	digital 3 digits		

Model	cost	pH range	mv range	recorder output	accuracy	reproducibility	smallest scale division	power	readout	temperature compensated	remarks
Devon Products Inc. (cont.)											
131	608	0-14			0.01pH			AC	digital 4 digits		
130	1092	0-14			0.001pH			AC	digital 5 digits	yes	
400	730	2-12		recorder included	0.1pH			AC	chart paper	0-100°C	
Ecologic Instrument Corp.											
102M	125	2-12					0.1pH	Bat	meter	0-100°C	
102	175	0-14			±0.1pH	±0.05pH		Bat	meter	0-100°C	
102D	475	0-14	±1999		0.01pH ±1mv			Bat AC	digital	0-100°C	
Enviro Monitor Inc.											
1001		2,5,10 or 14			±0.01pH						module for continuous monitor
501		2,5,10 or 14			±0.01pH					yes auto	module for continuous monitor
Fisher Scientific Co.											
Accumet 140	310	0-14	±700	yes	±0.1pH 615mv	±0.05pH ±5mv	0.1pH	AC	meter		
Accumet 150	320	0-14	±700	no	±0.1pH ±15mv	±0.05pH ±5mv	0.1pH	Bat	meter		

	Model	cost	pH range	mv range	recorder output	accuracy	reproducibility	smallest scale division	power	readout	temperature compensated	remarks
Fisher Scientific Co. (cont.)	Accumet 230	495	0-14	±1400	yes	±0.05pH ±14mv	±0.025pH ±5mv	0.1pH	AC	meter	0-100°C	ATC option
	expanded scale operation			±140		±1.4mv	±0.5mv					
	Accumet 291	675	0-14	±1999	yes	±0.02pH ±1.5mv	±0.01pH ±1.0mv	0.01pH	AC	digital 4 digits	0-100°C	ATC option
	Accumet 320	895	0-14	±1400	yes	±0.05pH ±5mv	±0.025pH ±2.5mv	0.01pH	AC	meter	0-100°C	ATC option
	expanded scale operation		any 1.4	±140		±0.005pH ±0,5mV	±0.0025 pH ±0.25mv					
	Accumet 420	925	0-14	±1999	yes	±0.01pH ±2mv	±0.01pH ±1.0mv	0.001pH	AC	digital 4 digits	0-100°C	ATC option
	expanded scale operation		6-8	±199.9		±0.002 pH ±0.2mv	±0.001 pH ±0.1mv					
	520	1250	0-14	±1400	yes	±0.002 pH ±0.2mv	±0.001pH ±0.1mV	0.001pH		digital 5 digits	0-100°C	ATC option
Hach Chemical Co.	16400	325	0-14	±700	yes	±0.14pH ±28mv		0.2pH 20mv	Bat	meter	0-100°C manual	also fluoride

Model	cost	pH range	mv range	recorder output	accuracy	reproducibility	smallest scale division	power	readout	temperature compensated	remarks
Hach Chemical Co. (cont.) expanded scale operation		any 2	200		±0.02pH ±4mv		0.02pH 2mv				
2075	189	0-14			±0.1pH	±0.05pH	0.1pH	Bat	meter	0-100°C manual	AC option
Horiba Instruments Inc. U-7		0-14			±0.1pH			Bat	digital	0-40°C auto	also measures temp.DO, cond. and turbidity
Instrumentation Laboratory Inc. 175 Porto-matic		0-14				±0.01pH	0.1pH	Bat	meter	0-100°C manual	Field use
Inter Ocean Systems, Inc. 500 CSTD O_2pHT		2-12				±0.1pH					Instrument measures cond., salinity temps depth
International Biophysics Corp. TRO pHY	275	0-14	±400	yes	0.1pH 5mv	0.1pH 5mv	2pH 10mv	Bat		0-100°C manual	
expanded scale operation		any 1.4pH	±40		0.3pH 2mv	0.02pH 1mv					
International Ecological Systems Corp. four function water analyzer		0-14	±700			0 05pH	0.1pH	AC Bat	meter	0-100°C manual	Instrument also monitors turbidity, temp, cond.

Model	cost	pH range	mv range	recorder output	accuracy	reproducibility	smallest scale division	power	readout	temperature compensated	remarks
Kernco Instruments Co. Inc.											
SS10	130	2-12						Bat	meter	0-100°C manual	
DS-40	152	2-12 4.5-9.5					0.1pH	Bat	meter	0-100°C	
KR-8	335	0-14	±700	0.05pH 5mv			0.1pH 10mn	AC	meter	0-100°C manual	ATC option
SR-15	650	2-12		recorder included	0.1pH			AC	chart pager	0-100°C	Bat option ATC option
expanded scale operation		4.5-9.5			0.05pH						
300	375	2-12		yes	0.02pH			AC	meter	0-100°C	ATC option
Kent Cambridge Instrument Co.											
7020		0-14	±1400	yes	±0.14pH		0.1pH	AC		0-100°C	ATC option
L.G. Nester Co.											
Mini pH meter	99	2-12			±0.15pH	±0.05pH	0.1pH	Bat	meter	0-100°C manual	
Digital Mini pH meter	170	0-14				±0.05pH	0.1pH	Bat		0-100°C manual	

	Model	cost	pH range	mv range	recorder output	accuracy	reproducibility	smallest scale division	power	readout	temperature compensated	remarks
La Motte Chem. Products Co.	HA	178	0-14			±0.1pH	±0.05pH		Bat	meter	0-100°C manual	
Leeds and Northrup	7417	370	0-14	0 to 1400	yes	±0.05pH ±10mv	±0.02pH ±2mv	0.1pH	Bat	meter	0-100°C	ATC option Nernst Corrector
	7411	439	0-14	±700	yes	±0.05pH ±7mv	±0.02pH ±2mv	0.1pH 10mv	AC	meter	0-100°C	ATC option
	7413	575	0-14	±1400	yes	±0.05pH ±7mv	±0.02pH ±2mv	0.1pH 10mv	AC	meter	0-100°C	ATC option Nernst Corrector
	expanded scale operation		any 2pH	any 200		±0.01pH ±1mv	±0.005pH ±0.5mv	0.01pH 1mv				
	7415	722	0-14	±1400	yes	±0.05pH ±7mv	±0.02pH ±2mv	0.1pH 10mv	AC	meter	0-100°C	ATC option Nernst Corrector
	expanded scale operation		any 1.4	any 140		±0.007 ±0.7mv	±0.002 ±0.2mv	0.001 1 mV				
	7421		0-14	±1400.0	yes	±0.002pH ±0.1mv	±0.001pH +0.1mv	0.001pH 0.1mv	AC	digital	0-100°C	ATC option Nernst Corrector
The London Co.	PHM 26	925	0-14	0 to 1400	yes		±0.01pH ±1mv	0.1pH 10mv	AC	meter	0-100°C	ATC option

Model		cost	pH range	mv range	recorder output	accuracy	reproducibility	smallest scale division	power	readout	temperature compensated	remarks
The London Co. (cont.)	expanded scale operation		any 1.4	0 to 140			±0.002 pH ±0.1mv	0.01pH 1mv				
	PHM 29	380	0-10 4-14	-300 to +700 +300 to -700		<0.05pH <5mv	±0.01pH ±1mv	0.1pH 10mv	Bat	meter	-10 to 100°C	AC power option
	PHM 61	415	0-14	±1400	yes	±0.03pH ±3mv	0.01pH 1mv	0.1pH 10mv	AC	meter		ATC option
	PHM 62	650	0-15	±1500	yes	±0.01pH ±1mv			AC	digital 4 digit	0-100°C	ATC option
	PHM 63	785	0-15	±1500	yes	±0.01pH ±1mv			AC	digital 4 digit	0-100°C	ATC option BCD output
	PHM 64	1195	0-15	±1500.0 ±5000	yes	±0.002 pH ±0.2mv			AC	digital 5 digit	0-100°C	ATC option BCD output
Markson Science Inc.	MA 4400	649	0-14	±1400	yes	±0.05pH ±7 mv	±0.02pH ±2 mv	0.1pH	AC	meter	0-100°C manual	measures conductivity
	expanded scale operation		any 1.4	140		±0.007 pH ±1 mv	±0.002 pH ±0.2mv	0.01pH				

	Model	cost	pH range	mv range	recorder output	accuracy	reproducibility	smallest scale division	power	readout	temperature compensated	remarks
	MA 4401	449	0-14	±1400	yes	±0.05pH ±7 mv	±0.02 pH ±2 mv	0.1pH	AC	meter	0-100 °C manual	
	expanded scale operation		any 1.4	140		±0.007 pH ±1mv	±0.002 pH ±0.2mv	0.01pH				
	MA 4403	798	0-14	±1999	yes	±0.007 pH ±1mv	±0.002 pH ±0.2mv		AC	digital	0-100 °C manual	also measures conductivity
	MA 4404	549	0-14	±1999	yes	±0.007 pH ±1mv	±0.002 pH ±0.2mv		AC	digital	0-100 °C manual	
Marteck Instruments Inc.	HMS	800	0-12 3-10.2		yes	±0.1pH			Bat	meter	auto	Intended for marine environment
Milton Roy	626.04		1-13		yes	±0.5%	<0.1pH	0.1pH	AC	meter	0-50 °C manual auto	designed for process control
	expanded scale operation	any 5pH					<0.05pH					
Moniteck	CT-515		2-12	±750				0.2pH	Bat	meter	0-100° C manual	Nernst corrector
	expanded scale operation	2-4,4-6 6-8 8-10, 10-12		±75	±0.04pH ±3mv							

Model	cost	pH range	mv range	recorder output	accuracy	reproducibility	smallest scale division	power	readout	temperature compensated	remarks
Orion Research Incorporated											
301	225	0-14	±400		±0.1pH	±0.04pH	0.2pH	AC	meter	0-100°C manual	
399A	460	0-14	±700	yes	±0.02pH	±0.5% of scale	0.1pH	AC	meter	0-100°C manual	Bat option ATC option
expanded scale operation		any 2.8			±0.004 pH	[illegible].5% of scale	0.02pH				
601	595	0-14	±1999	yes	±0.01pH	±0.01pH	0.01pH	AC	digital 4 digit	0-100°C manual	ATC option
701	895	0-14	±1999	yes	±0.01pH	±0.01pH	0.01pH	AC	digital	0-100°C manual	ATC option
expanded scale operation		any 2 from 3-11	±199.9		±0.001 pH	±0.001 pH					
801A	1295	0-14	±1999.9	yes	±0.002 pH	±0.001 pH	0.001pH	AC	digital	0-100°C manual	
Perkin Elmer Coleman Inst Division											
28B	259	0-14			±0.15pH	±0.02pH	0.1pH	AC	meter	0-100°C manual	
80	442	0-14	±1400		±0.15ph	±0.02pH	0.1pH	AC	meter	0-100°C manual	ATC option
expanded scale operation		any 3	300	yes	±0.03pH	±0.01pH	0.05pH				
37A	934	0-14	±1500		±0.005 pH		0.005	AC	null balance	0-100°C manual	

	Model	cost	pH range	mv range	recorder output	accuracy	reproducibility	smallest scale division	power	readout	temperature compensated	remarks
Perkin Elmer Coleman Inst. Div. (cont.)	38A	896	0-14	±1400	yes	±0.05pH	±0.01pH	0.05pH	AC	meter	0-100°C manual	ATC option
	expanded scale operation		any 1	100		±0.005 pH	±0.001 pH	0.005pH				
Photovolt	85A	198	0-14			±0.05pH	±0.05pH	0.1pH	AC	meter	0-100°C manual	
	115A	275	0-14	±400 ±800		±0.05pH	±0.03pH	0.1pH	AC	meter	0-100°C manual	
	126A	425	0-14	±400		±0.05pH	±0.01pH	0.1pH	Bat	meter	0-100°C manual	
	Expander IV	490	0-14	±1400	yes	±0.03pH	±0.02pH	0.1pH	AC	meter	0-100°C manual	ATC option
	expanded scale operation		any 4	140		±0.01pH	±0.005 pH	0.02pH				
	Digicord	725	0-14	±1400	yes	±0.002 pH	±0.002 pH	0.002	AC	digital	0-100°C manual	ATC option
	Aqucord	750	0-10 1-13	recorder built in	±0.05 pH	±0.025 pH		0.05pH		chart	0-130°C auto	Bat option

	Model	cost	pH range	mv range	recorder output	accuracy	reproducibility	smallest scale division	power	readout	temperature compensated	remarks
Pollutronics Inc.	PM-0	410	2-12	0-1000	yes	±0.02pH		0.2pH	AC	meter	0-100°C manual	
Research Appliance Company	2400		0-12		yes	1% of full scale					32°F-110°F auto	Industrial monitor
Sargent-Welch Scientific Co.	RB	110	0-14	±700		±0.15pH ±15mv	±0.02pH ±2mv	0.1pH 10mv	Bat	meter	0-100°C	
	IP	195	0-14	±1400		±0.1pH ±10mv	±0.01pH ±0.6mv	0.1pH 10mv	AC	meter	0-100°C manual	Nernst corrector
	PBL	315	0-14	±1000	yes	±0.1pH ±10mv	±0.02pH ±2mv		Bat AC	meter	0-100°C manual	ATC option Nerst correction
	PBX	425	0-14	±1400	yes	±0.1pH ±10mv			Bat AC	meter	0-100°C manual	ATC option Nernst correction
	expanded scale operation		any 0.7 any 1.4	140		±0.01pH ±0.005 pH	±0.01pH ±1mv					
	LS	450	0-14	±1400	yes	±0.05pH ±5mv	±0.01pH ±0.6mv		AC	meter	0-100°C manual	ATC option Nernst correction
	LSX	600	0-14	±1400	yes	±0.05pH			AC	meter	0-100°C manual	ATC option Nernst corrector

	Model	cost	pH range	mv range	recorder output	accuracy	reproducibility	smallest scale division	power	readout	temperature compensated	remarks
Sargent-Welch Scientific Co. (cont.)	expanded scale operation		any 1.4 any 0.7	140		±0.01pH ±0.005 pH	±0.01pH ±0.6mv					
	NX	575	0-14	±1999	yes	±0.01pH ±1mv	±0.01pH ±1mv	0.01pH 1mv	AC	digital 4 digit	0-100°C manual	ATC option Nernst corrector
Sensorex	310	125	0-14			0.1pH			Bat	meter		
Tekmar Instruments Inc.	BYK		0-14	±1999 ±199.9	yes			0.01pH	Bat AC	digital		ATC option designed for harsh environment
Weather Measure Corp.	FDM-1A	230	1-13			±0.1pH		0.2pH	Bat	meter	0-100°C manual	
	FHM-6A	550	0-14	±700	yes	±0.03pH ±5mv		0.1pH 10mv	AC	meter	0-100°C manual auto	
	expanded scale operation		3.5-10.5	±350	±0.015 pH ±2.5mv			0.05pH 5mv				
	FHM-7A	325	0-14	±700	yes	±0.05pH ±10mv			Bat AC	meter	0-100°C auto	

Model	cost	pH range	mv range	recorder output	accuracy	reproducibility	smallest scale division	power	readout	temperature compensated	remarks
Wheaton Scientific											
Single Range DC	245	0-14						Bat	meter	manual	Field use
Single Range ACDC	335	0-14						Bat AC	meter	0-100°C auto	Field use
Recording pH analyzer	1550			recorder included	±2% of full scale			Bat AC	chart	0-100°C auto	Field use

D. CONTENTS
FOR
TEMPERATURE
MONITORING INSTRUMENTATION

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A. INTRODUCTION

Temperature is a manifestation of the molecular kinetic energy within a body. The term temperature is generally used to denote the relative hotness or coldness of a body. In water quality monitoring, utilizations of temperature data include (a) use in calculation of the various forms of alkalinity, calcium carbonate saturation and stability studies, and other chemical studies. In limnologic studies, where temperatures of a water body are measured as a function of depth and other dimensions to determine suitability of habitat for fish and other aquatic life, (b) monitoring of thermal discharges from power plants, (c) to provide compensation to temperature-sensitive monitoring devices such as ion-selective electrodes.

The topic of water temperature is treated in a number of texts and articles. Those relating to parameters measured or to measurement procedures include, Standard Methods (Ref. 1), Methods for Chemical Analysis of Water and Wastes (Ref. 8), Water and Water Pollution Handbook (Ref. 20), and Instrumental Analysis for Water Pollution Control (Ref. 22). Selected references dealing with environmental effects of temperature changes in water include Water Quality Criteria (Ref. 2), Water Quality Criteria, 1968 (Ref. 6), "The Nation's Rivers" (Ref. 3), "Fuels Management in an Environmental Age" (Ref. 4), "Thermal Pollution in Unchartered Waters (Ref. 5), and "Biological Aspects of Thermal Pollution" (Ref. 7). A discussion of temperature compensation devices (usually thermistors) is found in literature sources such as Process Instruments and Controls Handbook (Ref. 10), and Mechanical Measurements (Ref. 15).

1. Applications of Water Temperature Measurements

The importance of the measurement of water temperature stems more or less directly from the effect of temperature on the rate of chemical reactions, on physical properties (surface tension, viscosity) and in a very complex way, on the rate of biological reactions. This leads to the influence of temperature at nearly every stage of water supply, extending even to the palatability of finished drinking water.

For the most part, temperatures of large water supplies (apart from thermal pollution) are beyond direct control because of the large energies involved (however, see Section 2). Nevertheless, control and predictability of treatment processes, maintenance of water quality in storage reservoirs, meeting requirements of industrial consumers--all these considerations have a significant temperature component. Contrary to most constituents and properties which can be controlled if necessary, temperature tends to be property to which processes must be tailored. Some typical aspects of water supply may be noted in which temperature plays an important, although not always well defined, role. Temperature regulation to meet the requirements of both water supply and recreational uses intensifies the need for close monitoring of temperature. Elevated reservoir temperatures also seem to be conducive to vigorous growths of the most undesirable algae.

Raw Water Storage: Seasonal temperature fluctuations in lakes and reservoirs are variable depending on geographical location, and especially on whether an ice-cover forms during the cycle. Most lakes and reservoirs, however, have in common a temperature stratification beginning in the spring, reaching a peak in mid or late summer, and disappearing in fall or early winter. During this stratification the surface waters are warmer (and subject to mixing) and the deeper waters are colder and quiescent. This thermal stratification causes chemical stratification, e.g., DO, nutrients, dissolved iron, manganese, etc. If outlet structures permit water withdrawal at various levels, some choice exists as to the temperature of the water withdrawn. Aeration by pumped air or water has in recent years been increasingly used to control water quality in raw water reservoirs. The principal object is to increase dissolved oxygen by altering or eliminating the temperature gradients.

Coagulation: "Coagulation describes the effect produced by the addition of a chemical to a colloidal dispersion resulting in particle destabilization by a reduction of the forces tending to keep the particles apart. The entire process occurs in a very short time, probably less than a second, and initially results in particles submicroscopic in size" (Ref. 28, p. 72). It would therefore appear that temperature effects are significant only in flocculation which is the formation of settleable particles from destabilized colloidal particles.

Flocculation: Theory holds the speed of flocculation to be determined by the number of contacts between floc particles in unit time, and to be directly proportional to the velocity gradient at a point (Ref. 29, p. 231). The same author has defined the mean velocity gradient as:

$$G_m = \sqrt{\frac{f}{\nu} \cdot \frac{V^3}{8R}}$$

where f = the friction factor (a function of the Reynolds number)
ν = the kinematic viscosity
V = the mean channel velocity over the cross-section
R = the hydraulic radius

"Since the value of ν for water is about doubled for a drop in temperature from 80° F. to the freezing point, Equation 27 indicates that the speed of flocculation will be reduced about 30 percent by this change in temperature" (Ref. 29, p. 233).

Support in the literature can be found for quite opposite effects of temperature on coagulation (flocculation) (Ref. 2, p. 283). This is understandable because results from full-scale coagulation plants are very difficult to interpret. Few, if any, operate at exactly the same rate of flow throughout the year and variations in such factors as turbidity, detention times, and dosages make it very difficult to isolate the effect of temperature alone.

Sedimentation: Temperature affects settling rates in two principal ways. The viscosity-temperature relation discussed under "flocculation" applies here, as a particle of given size, shape, and specific gravity will settle more slowly in a more viscous fluid. Additionally, temperature gradients will give rise to convection currents which will also disturb the rate of settling.

Filtration: Hudson (Ref. 30, p. 27-26) has presented an analysis of filter bed performance in which he incorporates a correction for water temperature implying that filter performance decreases with increasing temperature. It is likely that for the present, temperature dependence of filtration will have to be judged on empirical grounds. Ives (Ref. 31, p. K21), in a discussion of filtration theory, concludes:

> "These studies show why there is so little agreement among the published results of the dependence of filtration efficiency upon the various operating variables: particle size, grain size, flow rate, temperature, etc. A number of different transport mechanisms may operate simultaneously; their relative significances depend on the nature of the suspension as well as the operation of the filter."

Chlorination: "As a general rule, chlorine reacts with fewer materials as the pH increases, and with those materials with which it reacts the reaction rate increases with increasing temperature" (Ref. 28, p. 185).

"Low temperatures encountered in the winter season may require as much as a five-fold increase in contact time to equal the standard at summer temperatures" (Ref. 32, p. 436).

Monitoring: Instrumentation used to monitor water quality parameters can generate spurious signals which are due to changes in water temperature rather than to the pollutant or physical parameter being measured. For example, the voltage output of a pH electrode increases with increasing temperature. The temperature change can be compensated by including a thermistor in the appropriate part of the monitoring system. See Section C.3, entitled Thermistor.

2. Sources and Control of Temperature in Water

a. Natural Sources

Trees, vegetation, climatic conditions, and the mixing of lakes and streams control the temperature of a particular body of fresh, saline, or estuarine water. The temperatures of the surface waters of the United States vary from 0°C to over 38°C, depending on latitude, altitude, season, time of day, duration of flow, depth, and many other variables. The agents that affect the natural temperature are so numerous that it seems unlikely that two bodies of water, even in the same latitude, would have exactly the same thermal characteristics (Ref. 2). For example, the temperature variation along forested and unforested streams in Long Island, N.Y., were markedly different: a difference reflected by the absence or presence of forestation such as shade trees. See Table A-1 (Ref. 3). In another study, the removal of brush and trees along streams in the absence of urbanization was shown to cause an increase in the average maximum monthly temperature by 7.8°C (14°F) and to increase the annual maximum temperature from 14°C to 30°C (57°F to 85°F) (Ref. 3).

b. Man-Made Sources

Temperature changes in water relating directly to man's activities are attributable to thermal discharges from industry, municipal utilities, and land use such as landscaping or land clearance (see Section 2a, above).

Over 80% of all thermal pollution is said to arise from the generation of electricity (Ref. 4). For example, the Widow's Creek steam plant on the Tennessee River has a

Table A-1. Temperature variations and watershed characteristics of Long Island streams showing the effect of urbanization (Ref. 3).

Item	Rivers	
	East Meadowbrook	Connetquot
Drainage (ml)^2	31	24
Character	Urban	Forested
Vegetation along stream	Low	High
Temperature (°F)		
Mean of five stations		
June	66	60
January	42	42
Variation along stream		
June	10	0.5
January	2.0	1.0
Maximum range	17	28
Mean discharge (ft^3/sec)	~16.6	~38.8
Runoff	270%*	3%†

*Direct runoff increase 1937-1962;
†As stormwater, which was 3 percent of the total discharge.

capacity of 540 megawatts; the river has a flow of 47,000 cubic feet per second. The cooling water discharge from the steam plant causes a characteristic plume: "The maximum temperature difference at the discharge point is 10.3°F (5.7°C) and a temperature elevation about 1°F (0.6°C) exists at a distance about 1 mile downstream from the plant." See Table A-2 (Ref. 3).

"Generally, the amount of heat rejected to cooling water represents 45% of the heating value of the fuel used in the most efficient fossil fuel plants, and 55% in nuclear plants" (Ref. 4). On a comparative basis, about 50% more waste heat is rejected to the condenser cooling water from the nuclear plant than from the fossil fuel plant of the same electrical generation capacity Ref. 14). It is expected that by the year 2000 the steam electrical power industry will require 259,208 million gallons of fresh water daily versus 62,738 million in 1965 (Ref. 14). For saline waters, the projected requirement is 211,240 million gallons daily in 2000, versus 21,800 in 1965.

In summary, the source of temperature changes in water caused by man are primarily thermal discharges (over 80% of all thermal pollution) from electricity generating plants.

2. Deleterious Effects of Above Ambient Water Temperatures

Deleterious effects of higher than ambient temperatures in water can include the following (Refs. 5, 6, 7):

a. The capacity of the stream to assimilate wastes is decreased.
b. The dissolved oxygen content of the stream is decreased.
c. High temperatures can have lethal and sub-lethal effects on fish and other aquatic organisms (see Fig. A-1).
d. Drinking water temperatures of 15°C or higher are usually objectionable. 10°C is usually satisfactory, while above 19°C causes complaints from most consumers.

Temperature changes can affect aquatic life: The pumping rate of oysters increases with increasing temperature until at 30° to 35°C, the oyster is in distress. The low rate of pumping in cold water enables an oyster to avoid bacterial contamination from overlying waters so that the bacterial quality of the oyster is better than that of the water. Scallops accustomed to water between 5° and 20°C may be killed by sudden changes to temperatures of 21°C to 23°C (Ref. 2, page 285). Figure A-1 shows the effect of temperature changes on the rate of shell growth of a clam (Ref. 7).

Excessively high (or low) temperatures in irrigation water may affect crop growth and yields. A desirable range is 13° to 29°C (Ref. 6, page 118).

Additional information on deleterious effects of above ambient water temperatures is found in Water Quality Criteria by McKee and Wolf (Ref. 2), Water Quality Criteria (Ref. 6), and in the article by C.C. Coutant, "Biological Aspects of Thermal Pollution" (Ref. 7).

One beneficial aspect of high water temperature is reduced survival time for some infectious bacteria, cysts and ova of parasitic worms. Cultures of Leptospira in river water have survived for 9 days at 5° to 6°C, but for only 4 days at 31°C. Salmonella typhi and coliform organisms survive for longer periods at lower temperatures, and pathogenic organisms have survived for a year under ice. Schistosoma ova die in 9 days at 29° to 32°C, in three weeks at 15° to 24°C, and in three months or longer at 7°C (Ref. 2, page 283).

4. Water Quality Temperature Standards

The following is taken from Water Quality Criteria (Ref. 6, page 21):

> Surface water temperatures vary with geographical location and climatic conditions. Consequently no fixed criteria are feasible. However, any of the following conditions are considered to detract (sometimes

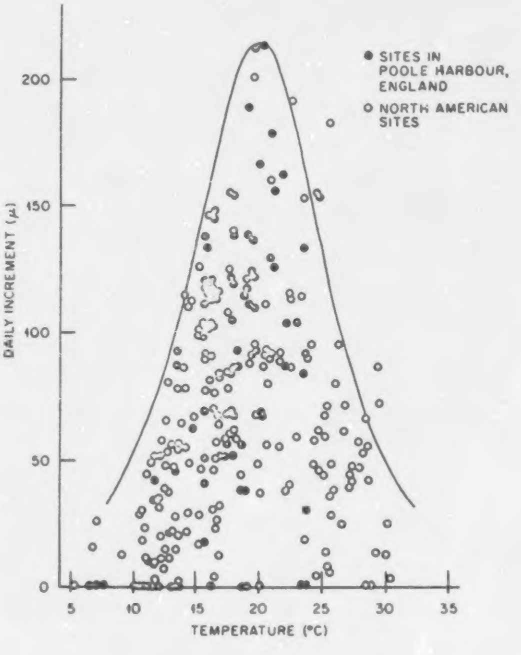


FIGURE A-1. The general relationship between temperature and rate of shell growth in the clam *Mercenaria mercenaria*, based on field measurements in England (solid) and North America (open) (Ref. 7).

Table A-2. Thermal effects: some TVA power plants (Ref. 3)

Total capacity (Mw)	River-flow (ft³/sec)	Velocity (ft/sec)	Cooling water discharge (ft³/sec)	Temperature increase (°F)		Effect on aquatic life
				Maximum (°F)	After mixing (°F)	
Widow's Creek, Guntersville Reservoir						
540	47,000	1.75	2,200	10.3	1	Diversity and abundance same above and below
Colbert, Pickwick Reservoir						
800	55,000	0.9	1,900	12		Discharge to Cane Creek; no significant effect on bottom organisms
Paradise, Green River above dam						
1,380	1,300	0.25	550	11 (controlled)		Relative abundance of fish reduced Summer periphyton growth rate down; winter, some rise Recovery 15 miles downstream Slime growth greatest near plant

seriously) from raw water quality for public water supply use:

(1) Water temperature higher than 85°F (29.4°C);

(2) More than 5°F water temperature increase in excess of that caused by ambient conditions;

(3) More than 1°F hourly temperature variation over that caused by ambient conditions;

(4) Any water temperature change which adversely affects the biota, taste, odor, or the chemistry of the water;

(5) Any water temperature variation or change which adversely affects water treatment plant operation (for example, speed of chemical reactions, sedimentation basin hydraulics, filter wash water requirements, etc.);

(6) Any water temperature change that decreases the acceptance of the water for cooling and drinking purposes.

Water intended for irrigation should not significantly influence the resultant soil temperature. Water Quality Criteria states, "Assuming that the soil temperature would not be lowered beyond that of a cold irrigation water, nor raised above that of a warm irrigation water, a desirable range of temperatures would be from 55° to 85°F (12.2° to 29.4°C) (Ref. 6, page 157).

For estuaries, Water Quality Criteria states:

In view of the requirements for the well-being and production of marine organisms, it is concluded that the discharge of any heated waste into any coastal or estuarine waters should be closely managed. Monthly means of the maximum daily temperatures recorded at the site in question and before the addition of any heat of artificial origin should not be raised by more than 4°F during the fall, winter, and spring (September through May), or by more than 1.5°F during the summer (June through August), north of Long Island and in the waters of the Pacific Northwest (north of California), summer limits apply July through September; and fall, winter, and spring limits apply October through June. The rate of temperature change should not exceed 1°F per hour except when due to natural phenomena.

Suggested temperatures are to prevail outside of established mixing zones as discussed in the section on zones of passage (Ref. 6, p. 35).

Additional information on criteria for water temperature can be found in Water Quality Criteria (Ref. 6), McKee and Wolf (Ref. 2), and in the article by C.C. Coutant entitled, "Biological Aspects of Thermal Pollution. II. Scientific Basis for Water Temperature Standards at Power Plants" (Ref. 7). The article by Coutant is of interest particularly because it treats the question of thermal standards for water bodies affected by power stations and partly because the author participated in the water quality revision project of the National Academy of Sciences, Environmental Studies Board (funded by the Environmental Protection Agency). The article is based on material prepared for use by that revision project. The revision is expected to be issued by the EPA in the fall, 1973.

B. TEMPERATURE DEFINITIONS

The temperature of waters is represented by a number; the establishment of a scale is merely the adoption of a set of rules for assigning a number to the temperature reading. For the sake of uniformity, standards exist for defining fixed points on temperature scales. Thes points are discussed in the sections which follow.

1. The measurement of temperature is based upon scales derived from the change of phase for certain elements and compounds which occur at fixed points. For example, the triple point of water is 273.16K. It is the temperature at which solid, liquid and vapor phases of water of highest purity coexist in equilibrium (Ref. 27, page 217). Other fixed points include the zinc point, tin point, antimony point, silver point, and gold point. Intermediate points are obtained by interpolation.

The first real step toward fabricating reliable thermometers with a reproducible scale was taken by Daniel Fahrenheit from 1706 to 1709 who perfected an alcohol-filled thermometer. By 1714, he was making mercury filled thermometers. Fahrenheit's scale was based on three fixed points: (1) zero was determined by immersing the bulb in a mixture of ice, water and sal ammoniac (ammonium chloride); (2) the second point, 32°, was obtained from a water-ice mixture; (3) the third point, 96° was the temperature determined by placing the thermometer bulb in the armpit of a "healthy" man. In 1742, Celsius, a Professor of Astronomy at Uppsala, proposed a scale with 0° for the boiling point of water and 100° for the melting point of ice. The definitions were later inverted, thereby obtaining the centigrade scale (see Ref. 9, page 2-4).

Measurements of water temperature are most often made using liquid-in-glass thermometers, thermocouples, thermistors, or resistance thermometers. More recent innovations include measurements using temperature sensitive oscillators, infrared radiation heat detectors, remote sensing, and digital readout. The user has options in terms of such factors as cost, sensitivity, simplicity, capability of continuous operation, and capibility of remote sensing. It would seem that the majority of water monitoring needs are met using liquid-in-glass thermometers, and a submersible sensor such as a thermistor or thermocouple. Specialized needs should be established on an individual basis: For example, thermal discharges are conveniently monitored using infrared sensors; remote and unattended sensing is possible using FM/FM telemetry.

2. Units

Units of temperature include Fahrenheit (°F), Réaumur, Celsius (°C) (Centigrade), Kelvin and Rankine (Ref. 9, section 2-4). The most commonly used in water monitoring are °F and °C, Fahrenheit and Celsius, respectively. Table B-1 shows data to convert °F to °C, or from °C to °F.

The relationship between the Fahrenheit and Celsius scales is defined to be:

$$T°C = \frac{5}{9}(F-32)$$

Some measurements or calculations used in water temperature monitoring use the Kelvin scale. The relationship between the Celsius and the Kelvin scales is

$$T,K = T°C + 273.15$$

3. Calibration of Temperature Sensors

Standard Methods, 13th edition (Ref. 1, page 348) and Methods for the Chemical Analysis of Water and Wastes (Ref. 8, page 296) note that for accurate readings, the good grade mercury-filled centigrade thermometer or thermistor should be checked against a precision thermometer certified by the National Bureau

Table B-1. Look up the known temperature in center column (between °F and °C). The equivalent temperature in either °F or °C can then be found in the appropriate column.

°F.		°C.	°F.		°C.	°F.		°C.
+ 32.0	± 0	—17.78	230.0	110	43.33	428.0	220	104.44
+ 35.6	+ 2	—16.67	233.6	112	44.44	431.6	222	105.56
+ 39.2	+ 4	—15.56	237.2	114	45.56	435.2	224	106.67
+ 42.8	+ 6	—14.44	240.8	116	46.67	438.8	226	107.78
+ 46.4	+ 8	—13.33	244.4	118	47.78	412.4	228	108.89
+ 50.0	+10	—12.22	248.0	120	48.89	446.0	230	110.00
+ 53.6	+12	—11.11	251.6	122	50.00	449.6	232	111.11
+ 57.2	+14	—10.00	255.2	124	51.11	453.2	234	112.22
+ 60.8	+16	— 8.89	258.8	126	52.22	456.8	236	113.33
+ 64.4	+18	— 7.78	262.4	128	53.33	460.4	238	114.44
+ 68.0	+20	— 6.67	266.0	130	54.44	464.0	240	115.56
+ 71.6	+22	— 5.56	269.6	132	55.56	467.6	242	116.67
+ 75.2	+24	— 4.44	273.2	134	56.67	471.2	244	117.78
+ 78.8	+26	— 3.33	276.8	136	57.78	474.8	246	118.89
+ 82.4	+28	— 2.22	280.4	138	58.89	478.4	248	120.00
+ 86.0	+30	— 1.11	284.0	140	60.00	482.0	250	121.11
+ 89.6	+32	± 0.00	287.6	142	61.11	485.6	252	122.22
+ 93.2	+34	+ 1.11	291.2	144	62.22	489.2	254	123.33
+ 96.8	+36	+ 2.22	294.8	146	63.33	492.8	256	124.44
+100.4	+38	+ 3.33	298.4	148	64.44	496.4	258	125.56
+104.0	+40	+ 4.44	302.0	150	65.56	500.0	260	126.67
107.6	42	5.56	305.6	152	66.67	503.6	262	127.78
111.2	44	6.67	309.2	154	67.78	507.2	264	128.89
114.8	46	7.78	312.8	156	68.89	510.8	266	130.00
118.4	48	8.89	316.4	158	70.00	514.4	268	131.11
122.0	50	10.00	320.0	160	71.11	518.0	270	132.22
125.6	52	11.11	323.6	162	72.22	521.6	272	133.33
129.2	54	12.22	327.2	164	73.33	525.2	274	134.44
132.8	56	13.33	330.8	166	74.44	528.8	276	135.56
136.4	58	14.44	334.4	168	75.56	532.4	278	136.67
140.0	60	15.56	338.0	170	76.67	536.0	280	137.78
143.6	62	16.67	341.6	172	77.78	539.6	282	138.89
147.2	64	17.78	345.2	174	78.89	543.2	284	140.00
150.8	66	18.89	348.8	176	80.00	546.8	286	141.11
154.4	68	20.00	352.4	178	81.11	550.4	288	142.22
158.0	70	21.11	356.0	180	82.22	554.0	290	143.33
161.6	72	22.22	359.6	182	83.33	557.6	292	144.44
165.2	74	23.33	363.2	184	84.44	561.2	294	145.56
168.8	76	24.41	366.8	186	85.56	564.8	296	146.67
172.4	78	25.56	370.4	188	86.67	568.4	298	147.78
176.0	80	26.67	374.0	190	87.78	572.0	300	148.89
179.6	82	27.78	377.6	192	88.89	590.0	310	154.44
183.2	84	28.89	381.2	194	90.00	608.0	320	160.00
186.8	86	30.00	384.8	196	91.11	626.0	330	165.56
190.4	88	31.11	388.4	198	92.22	644.0	340	171.11
194.0	90	32.22	392.0	200	93.33	662.0	350	176.67
197.6	92	33.33	395.6	202	94.44	680.0	360	182.22
201.2	94	34.44	399.2	204	95.56	698.0	370	187.78
204.8	96	35.56	402.8	206	96.67	716.0	380	193.33
208.4	98	36.67	406.4	208	97.78	734.0	390	198.89
212.0	100	37.78	410.0	210	98.89	752.0	400	204.44
215.6	102	38.89	413.6	212	100.00	770.0	410	210.00
219.2	104	40.00	417.2	214	101.11	788.0	420	215.56
222.8	106	41.11	420.8	216	102.22	806.0	430	221.11
226.4	108	42.22	424.4	218	103.33	824.0	410	226.67

of Standards. Thermometers are calibrated by

Thermometry Laboratory
Heat Division
National Bureau of Standards
Washington, D.C. 20234

Accurate temperature readings are important in studies involving aquatic life. For example, Fig. A-1 shows the rate of shell growth changes markedly over small temperature ranges.

C. METHODS FOR TEMPERATURE MEASUREMENT

Temperatures of water measurements are made by a variety of methods. Any good grade of mercury-filled thermometer is satisfactory for applications not involving unattended operation. Thermistors or resistance thermometers are used for unattended operation such as continuous monitoring or remote sensing. Infrared sensors are used for non-contact measurements of water surface temperatures.

1. Liquid-in-Glass Thermometers

Galileo is generally credited with inventing the thermometer about 1595: His first thermometers were glass bulbs on long stems, with the stem ends immersed in water. The first sealed thermometers contained alcohol as the liquid and were made before 1654. Mercury-filled glass thermometers were being made by Daniel Fahrenheit in 1714 (Ref. 9, page 2-5).

Besides alcohol or mercury, liquids used in glass thermometers include gallium, mercury-thallium, toluol, pentane, and silicones (Ref. 10). A typical glass thermometer with bare bulb is shown in Figure C-1, and a sectional view of an industrial thermometer is shown in Figure C-2. Figure C-3 shows typical response curves for industrial thermometers, including covered and uncovered bulbs.

Organic liquids have a much larger temperature coefficient than mercury so larger diameter capillary tubes can be used to provide easier reading. The space above the liquid is generally filled with a gas; dry nitrogen is commonly used for mercury thermometers (Ref. 11).

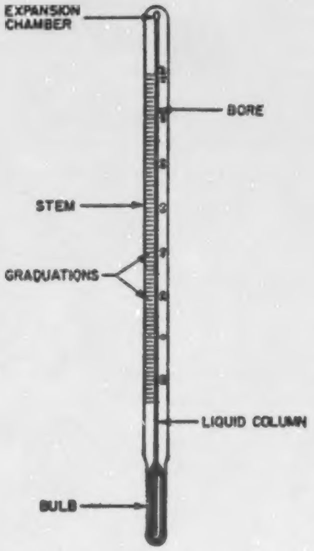


FIG. C-1. Typical all-glass thermometer. Calibrated scale is etched on the stem (Ref. 10, p. 2-89).

Liquid-in-glass thermometers are used in three ways: (1) total immersion (usually without markings on the back pertaining to immersion) in which the bulb and all of the liquid column is immersed; (2) partial immersion where the bulb and an indicated inscribed portion of the column is immersed; (3) complete immersion where the entire thermometer is submerged in the water (they bear the incription "complete immersion" on the back). Attention to the proper immersion depth is important because erroneous readings can be obtained from improper use. Total immersion thermometers are recommended for the most accurate temperature determinations with partial immersion thermometers recommended for use when total immersion is not feasible (Ref. 12).

Mercury is the ideal thermometer liquid because it can be produced with an extremely high degree of purity, is not subject to significant contamination or deterioration if properly handled, is stable under the influence of high temperatures, expands almost linearly with temperature increases, and does not wet glass. Organic filling liquids are deficient in some or all of these aspects. Disadvantages of mercury are that the lowest measurable temperature is limited by its freezing point to -38.87°C, and its low coefficient of expansion (Ref. 11). Neither disadvantage is of large importance for water monitoring.

Liquid-in-glass thermometers have a variety of shapes and are fabricated to cover different temperature ranges and tolerances. Selected information is shown in Table C-1 for some thermometers (Ref. 13). Disadvantages of thermometers include fragility and that they cannot be used for remote sensing or unattended operation.

Additional information on liquid-in-glass thermometers can be obtained from Process Instruments and Controls Handbook (Ref. 10) and the excellent articles by Thompson (Ref. 11) and Ween (Ref. 12).

2. Resistance Thermometers

The resistance thermometer depends upon the change in electrical resistivity of metals when they undergo a change in temperature. Metallic conductors such as Pt, Cu, Ni, Ag are used as industrial thermometer bulbs. The actual relationship between the temperature of water and the resistance of the metal employed must be determined experimentally. However, for most metals the following empirical equation holds very closely (Ref. 15, page 453):

$$R_t = R_o\ (1 + AT + BT^2)$$

R_t = Resistance at temperature T

R_o = Resistance at 0°F

T = Temperature, °F

A and B = Constants depending on metal

(Fig. C-6 shows the variation in specific-resistance of Pt, with temperature.)

Figure C-4 shows the general construction of a Foxboro Co. element: Heat is transferred quickly from the end flange through the silver core to the metal wire resistance winding. The ceramic insulator terminal provides good electrical insulation between the coils of the resistance wiere while also providing minimal thermal insulation to insure quick response to temperature changes. Table C-2 shows some properties of resistance-thermometer elements: Note that the response time can range up to 60 sec. for Ni as the element in a brass case material.

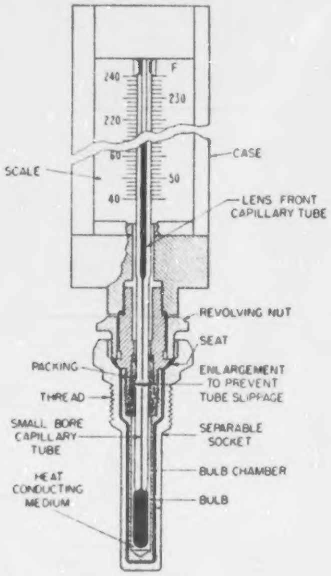


FIG. C-2. Sectional view of industrial thermometer (Ref. 10, p. 2-91).

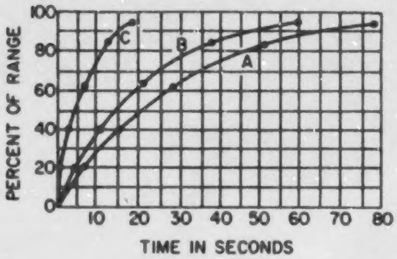


FIG. C-3. Response curves for typical industrial thermometers: (A) with tapered socket, (B) with socket removed, (C) with bulb chamber removed (bulb bare) (Ref. 10).

Resistance, and thus temperature, measurements are commonly made using a bridge-type circuit. A simple arrangement in which the element comprises one arm of a Wheatstone bridge is subject to error because the resistance of the lead wires connecting the element to the bridge is included in the reading. Figure C-5 shows a bridge schematic utilizing three leads from the element, which compensates for the effect of lead wire resistance. Leads a and c in the circuit shown are connected directly to one end of the resistor bulb winding at a common point; the third lead b is connected to the other end of the winding. One of the leads is connected to c which brings this lead directly to the bulb winding. Hence, the resistance of lead a is added to bridge arm R_1 while the resistance of lead b is added to bridge arm R_X, thus dividing the lead resistance and retaining a balance in the bridge circuit. The ultimate accuracy of the circuit depends upon leads a and b being of equal resistance. Increased accuracy can be obtained using four leads. The interested reader is referred to Ref. 10, page 2-56, and Ref. 15, page 456, for further details.

3. Thermistor

Thermistors are prepared from semiconductor materials such as oxides of manganese, nickel, and cobalt. Unlike metals, the resistance varies inversely with temperature, as shown in Figure C-6. Thermistors have excellent sensitivity and a fast response to temperature changes (e.g., 3 seconds for standard thermistors to milliseconds for flake thermistors). However, the thermistor temperature monitors may show an aging effect which could cause erroneous readings. See Figure C-7.

The temperature-resistance function for a thermistor is given by the relationships (Ref. 15):

$$R = R_o e^k$$

and

$$k = \beta\left(\frac{1}{T} - \frac{1}{T_o}\right)$$

Table C-1. Specifications table of some total immersion thermometers available from Arthur H. Thomas (Ref. 13).

THERMOMETERS, Centigrade*

Graduated stem, scaled in centigrade degrees. Calibrated for total immersion. Meet requirements of U.S. National Bureau of Standards Circular No. 600, but certificate is not supplied.

Filled with nitrogen above the mercury column. Thermometers have white backgrounds and stems 6 to 7 mm o.d.

Range	Interval	Tolerance	Length	Approximate Price
−10 to +101°C	1°	±0.5°	300 mm	5.30
−10 to +101°C	1/2°	±0.5°	350 mm	7.25
−10 to +101°C	1/5°	±0.4°	400 mm	12.10
−10 to +101°C	1/10°	±0.3°	650 mm	17.00
−10 to +250°C	1°	T1	350 mm	7.00
−10 to +250°C	1/2°	T1	400 mm	8.80
−5 to +360°C	1°	T2	400 mm	7.90
−5 to +360°C	1/2	T2	500 mm	13.90
−5 to +500°C	1°	T2	500 mm	15.85

T1 equals ±0.5° to 100° and ±1° above 100°.
T2 equals ±2° to 300° and ±4° above 300°.

*Preferred usage is: Celsius.

in which R = resistance at any temperature T, °K,

R_o = resistance at reference temperature T_o, °K,

β = a constant.

The application of thermistors to the measurement of temperature follows the usual principles of resistance thermometry. A conventional bridge or other resistance-measuring circuit is commonly employed. The high temperature coefficient of thermistors results in their having greater available sensitivity as temperature-sensing elements than metal resistance thermometers or common thermocouples. To illustrate, the use of thermistors permits the adaptation of conventional temperature recorders to the measurement of 1°C spans, which is not feasible with ordinary resistance-thermometers or thermocouple elements.

As with any resistance thermometer, consideration must be given to keeping the measuring current sufficiently small in order that the element resistance shall be dependent upon the temperature of the surroundings and not the internal heating of the sensor itself. The average power dissipation can be reduced without sacrificing sensitivity by energizing the thermistor element with pulses.

Thermistors are readily designed for sufficiently high resistance values to make lead-resistance errors negligible. Hence, thermistor primary elements, unlike metallic resistance thermometers and thermocouples, can be located remotely from their associated measuring circuits. This permits greater flexibility in application.

Lathrop and Jones described an elegant water temperature monitor using complimentary metal oxide semiconductor (C/MOS) integrated circuits (Ref. 26). The battery powered instrument is housed in a buoy and requires no external electrical connections. Temperature is periodically sampled and stored in Large Scale Integration (LSI) shift register circuits. Depending on the frequency of temperature sampling, data may be stored from days to weeks if desired. The measurement range is from 0°C to 50°C with an accuracy of ±0.1°C. This is accomplished using a temperature sensitive C/MOS oscillator. See Fig. C-8.

Besides temperature measurements, thermistors are widely used as "built-in" temperature compensators for other measuring instruments such as dissolved oxygen sensors. Here, advantage is taken of the negative coefficient of resistance. For example, in the case of a copper-wire meter movement, the resistance increases about 0.4%/°C. A thermistor with about one-tenth the resistance of the copper and with a temperature coefficient of -4.0%/°C, placed in series with the meter, would serve to make the overall resistance constant over a small temperature range. Of course, the thermistor must be placed so that it is exposed to the same temperature as the measuring sensor (Ref. 10, p. 2-66).

4. Thermocouple

In 1826 Thomas J. Seebeck discovered that an emf could be produced by purely thermal means in a circuit composed of two different metals whose two junctions are maintained at different temperatures. The two metals constitute a *thermocouple*. When the temperature of one junction (the reference junction) is kept constant, the emf is found to be a function of the temperature of the other junction (the

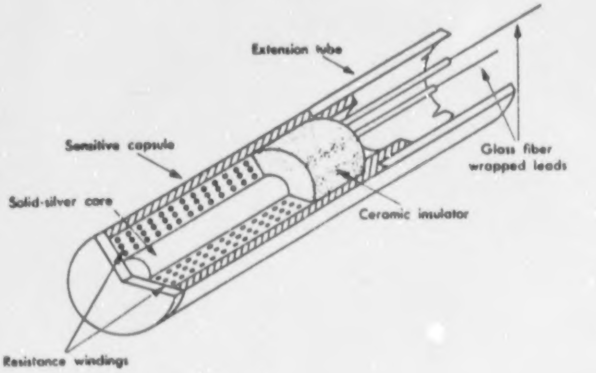


FIGURE C-4. Sections illustrating construction of resistance thermometer elements (Ref. 15, p. 454).

Table C-2. Typical properties of Resistance-Thermometer Elements (Ref. 15, p. 455).

Type of element	Case material	Temperature range, °F	Resistance, ohms	Sensitivity, ohms/°F (approx.)	Limits of error, °F	Response,* sec
Platinum (laboratory)	Pyrex glass	−300 to 1000	25 at 32°F	0.05	±0.02	—
Platinum (industrial)	Stainless Steel	−325 to 250†	25 at 32°F	—	±1.5	10 to 30
		0 to 1000‡	25 at 32°F	—	±3	10 to 30
Copper	Brass	−100 to 250	10 at 77°F	0.2	±0.75	20 to 60
Nickel	Brass	32 to 250	100 at 68°F	—	±0.5	20 to 60

* Time required to detect 90% of any temperature change in water moving at 1 fps. The lower value is for the thermometer in a case only, while the higher value is for the thermometer in a protective well.

† Low range.

‡ High range.

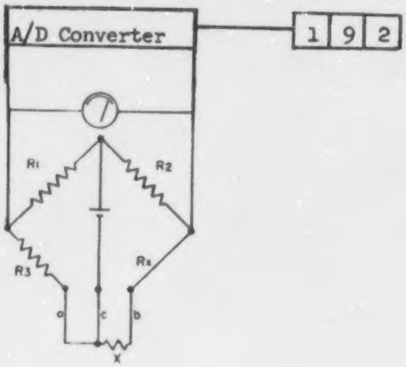


FIG. C-5. Three-lead method for connecting resistor bulb to measuring instrument. Both analog (meter) and digital (numerical) display shown (Ref. 10).

test junction). This fact enables the thermocouple to be used as a thermometer. An advantage of a thermocouple thermometer is that, because its heat capacity is small, the test junction comes quite rapidly to thermal equilibrium with the system whose temperature is to be measured. It therefore follows temperature changes easily.

If two different materials are joined to form *only one junction*, and if a current is sent through the junction while it is maintained at constant temperature, a heat flow will take place between the junction and its surroundings, called the *Peltier heat*, after its discoverer, Jean C. A. Peltier.

In a single wire whose ends are maintained at different temperatures, the free electron density varies from point to point. Each element of a wire of nonuniform temperature is therefore a source of voltage, a discovery made by Sir William Thomson (Lord Kelvin). When a current is maintained in a wire of nonuniform temperature, heat is liberated or absorbed at all points of the wire, and this *Thomson heat* is proportional to the quantity of electricity passing the section of wire and to the temperature difference between the ends of the section.

"...The Seebeck emf E_{AB} of a thermocouple is the resultant of two Peltier emf's $(\pi_{AB})_t$ and $(\pi_{AB})_{t_R}$, and two Thomson emf's, $\int_{t_R}^{t} \sigma_A dt$ and $\int_{t_R}^{t} \sigma_B dt$. The relation among these emf's is the *fundamental thermocouple equation:*

$$E_{AB} = (\pi_{AB})_t - (\pi_{AB})_{t_R} + \int_{t_R}^{t} (\sigma_A - \sigma_B) dt$$

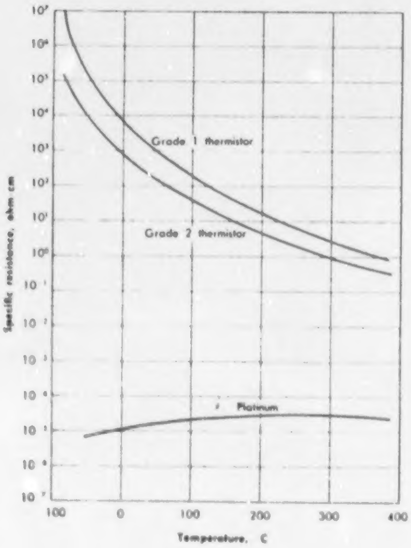


FIG. C-6. Typical thermistor temperature-resistance relations.

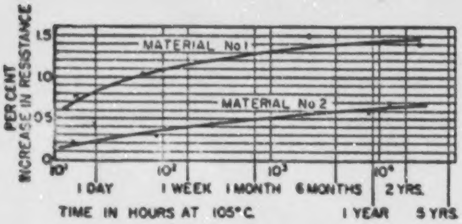


FIG. C-7. Change in thermistor resistance versus time at 105°C (Ref. 10).

The sign conventions is this equation are:

1) E_{AB} is positive when the direction of the thermocouple current is from A to B at the test junction, which is to be taken to the *warmer* of the two junctions.

2) π_{AB} is positive when the current is from A to B and Peltier heat is *absorbed* by the junction.

3) σ_A is positive when the current is opposite to the direction of the temperature gradient (low to high temperature) and Thomson heat is *absorbed* (Ref. 27, page 404).

For practical application, one junction is used as a reference potential and held at a constant temperature of known value (usually ice-water). The temperature of the second junction which is immersed in the water sample is found by measuring the potential and referring to calibration tables to find the temperature difference. Figure C-9 shows a schematic measuring system. Table C-3 lists some operating parameters for the bi-metallic combinations most commonly used in the United States.

The user should take care not to bend, cold work, flex, or otherwise deform the thermocouple wire, as this may affect the accuracy. Unwanted thermocouple junctions are created when adding leads to a thermocouple circuit, or connecting the sensor to a recorder. False readings can be avoided by maintaining a uniform ambient temperature in the vicinity of extraneous junctions and at the measuring device. Oxidizing or corrosion conditions gradually degrade the metal wires. Finally, the thermocouple must be permitted to stabilize after temperature changes; this may be require several seconds (Ref. 17).

5. Digital Thermometers

Digital thermometers use conventional sensors coupled with analog to digital (A/D) converters, to display temperature readings in numerical form. Although more expensive, digital readout may be favored over analog readout if, for example, reading accuracies of greater than 1% are desired, because it is often more practical to transmit, store, and record digital information than analog information and it is usually difficult to display information in analog form with better than 1% resolution. Digital display may also be favored as a means of minimizing operator error such as converting from a microvolt reading to the equivalent temperature. Reference 23 contains additional information on analog-digital tradeoffs.

Figure C-10 is a block diagram schematic of a Doric Scientific digital thermocouple instrument. The temperature change is sensed at the measuring junction ("hot" junction) relative to the reference junction ("cold" junction). The potential difference between the two junctions is amplified, undergoes A/D conversion, and the resulting digital reading is converted to a temperature reading before being displayed numerically.

It is necessary that the reference junction maintain a constant value because any drift will cause erroneous readings. The Doric digital instruments use a solid-state electronic compensator instead of an ice-bath to simulate the reference temperature/voltage. This compensator is possibly more convenient than an ice-bath but should be checked occasionally for any aging effects with the standard ice-bath.

A/D conversion is accomplished using a dual slope integrating technique. See Figures C-11 and C-12. The basic idea of the dual integration technique is to generate a pulse width proportional to the analog input voltages by making a time comparison between two integrations. In this way, many of the absolute errors in generating the integrated ramp voltage are eliminated.

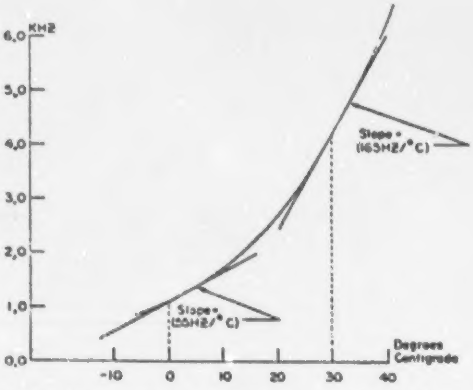


FIG. C-8. Typical frequency variation vs. temperature (Ref. 26).

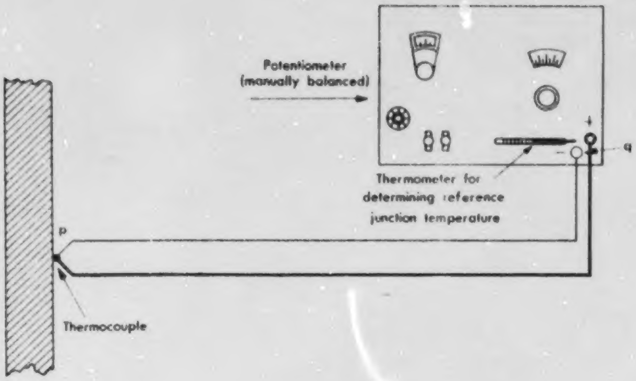


FIG. C-9. Schematic diagram illustrating use of potentiometer terminals as a reference junction (Ref. 15).

Thermocouple Type	ISA Code	Nominal Temp Range (°F)	Limits of Error**		Suitable Environments	Nominal Output µv/°F		Nominal Cost*
			Standard Grade	Special Grade		32°F	1000°F	
Plat 6% Rhodium/ Plat. 30% Rhodium	B	1200 to 3000	±½ %	–		0	3	$20-40
Chromel/ Constantan	E	32 to 600 600 to 1600	±3°F ±½ %	–	Vacuum, inert, oxidizing, reducing may be used below 0°F	31	45	$5-15
Iron/Constantan	J	32 to 530 530 to 1400	±4°F ±¾ %	±2°F ±⅜ %	Vacuum, inert oxidizing or reducing avoid H_2 at high temp. Brittle at sub-zero temp	30	40	$5-15
Chromel/Alumel	K	32 to 530 530 to 2300	±4°F ±¾ %	±2°F ±⅜ %	Inert or oxidizing not for reducing atmosphere	20	26	$5-20
Platinum/Platinum 13% Rhodium	R	32 to 1200 1200 to 2700	±5°F ±½ %	±2.5°F ±¼ %	Easily contaminated Use in non-metallic silica free tube Use in inert or oxidizing atmos. but not reducing atmos. vacuum for short periods	3	8	$15-30
Platinum/Platinum 10% Rhodium	S					3	5	$15-30
Copper/Constantan	T	−300 to −75 −150 to −75 −75 to +200 200 to 700	– ±2% ±1½°F ±¾ %	±1% ±1% ±¾°F ±⅜ %	Vacuum, inert oxidizing or reducing excellent for sub-zero temp.	21	–	$5-15

*Nominal cost for 12" sheathed thermocouple from t/c manufacturers
**When the limit of error is given in %, the percentage applies to the temperature being measured, not the ranges

Table C-3. Limits of error for commonly used thermocouples (Ref. 24).

The first integration is performed on the voltage from the hot junction: It proceeds for the fixed time interval, T_1. The input to the operational amplifier is then switched to the reference potential of opposite polarity. The time from this switching until the integrator output reaches some fixed reference point gives a measure of the analog input voltage. From time T_1 until the integrator output has reached the known reference voltage, counts from a source of clock signals are entered in a binary counter. The final count in the register is then the digital equivalent of the input analog voltage.

The Doric instrument digitizes the voltage signal from the thermocouple and digitally corrects the internal counter for direct display in degrees of temperature. A digital computing technique with read-only memory performs the linearization function. The read-only memory stores the conversion look-up tables (made up by using data from the National Bureau of Standards) to allow direct temperature display from the digitized millivolt signal data. Digital correction is obtained without resorting to variable gate time or clock oscillator variation techniques and their inherent drawbacks. Digital linearization for the Doric instrument is accomplished using a 32 segment binary rate multiplier in which each segment has a resolution of one part in 511 (9 digital bits).

6. Other

a. Semiconductor Sensors

Commonly used temperature transducers (thermistors, thermocouples, resistance thermometers) are all nonlinear: They are restricted to narrow ranges or require complex calibration charts or linearizing circuits for use outside the linear range.

Pease has suggested semiconductor sensors such as FD200 silicon diodes for use as a linear temperature transducer (Ref. 18). These elements have forward voltages of about 600 mV at room temperature and relatively constant temperature coefficients in the range of about -2 mV/°C to -3 mV/°C. As additional attractions, the components are said to be inexpensive, reliable, stable, compact, and to provide a fairly fast response. Figure C-13 shows a linear silicon diode thermometer using an operational amplifier circuit in which the current through the silicon diode sensor is determined primarily by the voltage, $-V_{Ref}$, and the precision resistor R1. Resistors R2 and R3 balance out the nominal forward voltage drop of the diode while R5 and R6 are used to zero the amplifier output at the temperature of reference. With the values shown in Figure C-13, the sensitivity is calculated to be +100 mV/°C; by comparison, a thermocouple has a sensitivity of only 40 to 50 µV/°C. However, V_{Ref} must be stable.

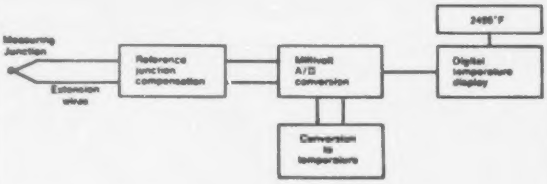

Measuring Junction
Extension wires
Reference junction compensation
Millivolt A/D conversion
Conversion to temperature
2486°F
Digital temperature display

FIG. C-10. Schematic of digital thermometer (Ref. 24).

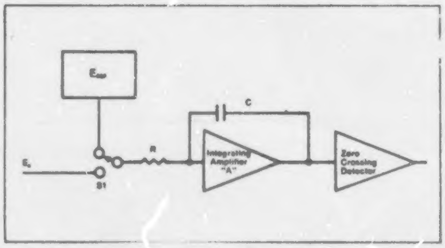


FIG. C-11. Basic dual slope technique (Ref. 24).

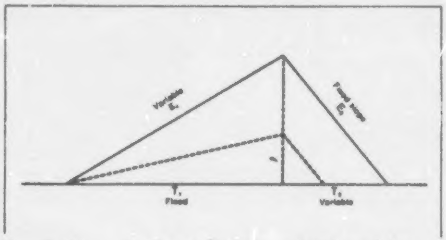


FIG. C-12. Voltage/time relationship (Ref. 24).

b. Acoustic Telemetry--Remote Measurements

Telemetry is the technique of measuring a quantity and transmitting the result to a distant location. Data transmission may be via telephone lines or microwave or radio frequency links. The advantages of telemetering data over recording of data at the source include the following:

(1) The weight of telemetering equipment located at the data source is usually less than that of recording equipment of comparable capacity;

(2) Besides temperature, a number of other sensors may be monitored continuously without requiring operator attention;

(3) In case of instrument failure, data are recorded right up to the final moment;
(4) Recording time is not limited by the capacity of a data storage device;
(5) Sensors can monitor waters that may become inaccessible due, for example, to heavy snow or other inclement weather; and
(6) Data may be recorded in a real time mode.
These positive factors must be weighed by a potential user with the disadvantages of telemetry. Telemetering of data is more complex; leased telephone lines are expensive and radio links are costly to maintain. Additional sources of extaneous error may be introduced along the transmission path.

Nuclear Division, Union Carbide Corporation, has developed a temperature-sensitive implantable fish tag based on a thermistor. It is used to measure either the body temperature of fish or brought outside the fish to measure water temperature. The tags transmit acoustic energy at frequencies between 65 and 100 kHz, are pulse-period modulated and battery powered (Ref. 19). The effective range for temperature telemetry extends to 500 yards. It covers a temperature range of 5° to 35°C with an expected accuracy of ±0.2°C.

The acoustical modulated signal can be decoded using commercially available instrumentation by interfacing the receiver output with a frequency counter to measure the pulse period.

A very good discussion of monitor[illegible]sing telemetry is given by McNelis in Wate[illegible] Water Pollution Handbook, Vol. 4 (Ref. 20).

c. Infrared Sensors

The use of infrared (IR) radiation provides a very practical method for making remote, noncontact, and rapid measurements of the surface temperature of water. Between 4 to 12.5 μm, the emissivity of the ocean surface is 0.98 for radiation normal to the surface (Ref. 25, page 382), and the IR radiation characteristics closely approach those of a black body at 27°C. Figure C-14 shows the spectral-radient emittance corresponding to two temperatures (-2°C and 35°C) calculated on the basis of black body radiation. The major portion of energy for this range of temperatures is included in the region 6 to 20 μm (Ref. 25).

The principle of these sensors is described by the Stefan-Boltzmann law that states the intensity of the radiation emitted by an object is dependent on the temperature of the object. Mathematically, for an emitter,

$$W = E\sigma T$$

W = the total energy emitted from the surface, $\text{erg/cm}^2\text{/sec}$
σ = Boltzman constant, 1.38×10^{-16} erg/deg
T = temperature
E = emissivity (for water, $E = 0.95$ to 0.993, over the range 8 to 14 μm)

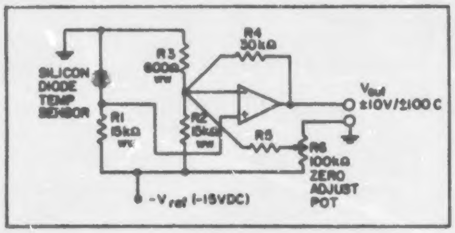


FIG. C-13. Linear thermometer based on silicon diode sensor (Ref. 18).

The Wahl Heat Spy Monitors using infrared temperature sensing are reported by the manufacturer to have a 0.5°F temperature resolution. Figure C-16 shows the optical diagram for the Wahl Model HSM-500 (Ref. 21). Infrared radiation from the water stream being monitored is collected by a lens, modulated by a chopper, and focused onto a thin film thermistor detector through an optical filter. The detector converts the infrared radiation into an electrical signal which is subsequently amplified, demodulated, and read out on a meter in °F.

The Wahl Model HSA-150A can be used for water thermal pollution measurements because it covers the range -20°C to +60°C. The optical diagram is similar to that shown in Figure C-15. Heat detection is by means of a chopped thermistor bolometer. (Bolometers transduce IR radiation into an electrical signal utilizing the change in resistance with temperature of a thermistor. A Wheatstone bridge circuit is commonly used.)

Mancy has used laboratory-built infrared monitoring instrumentation to measure water temperature and thermal effluent discharges (Ref. 22, pages 174, 182). Measurements were made from an airplane and clearly show effects such as those of wind velocity and direction on thermal discharge plumes from a power plant into Lake Michigan.

Further information on IR temperature-of-water monitoring may be obtained from

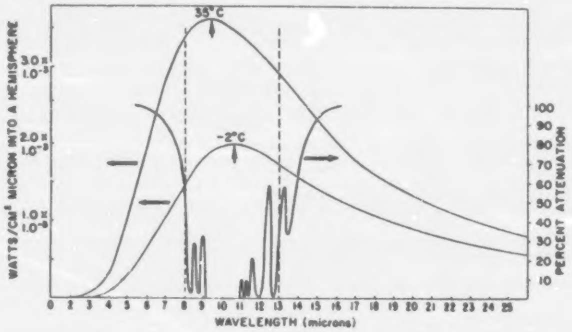


FIG. C-14. Blackbody distribution (Planck law) for -2°C (271°K) and +35°C (308°K), and atmospheric attenuation of 1000 ft. of air path at sea level (Ref. 25).

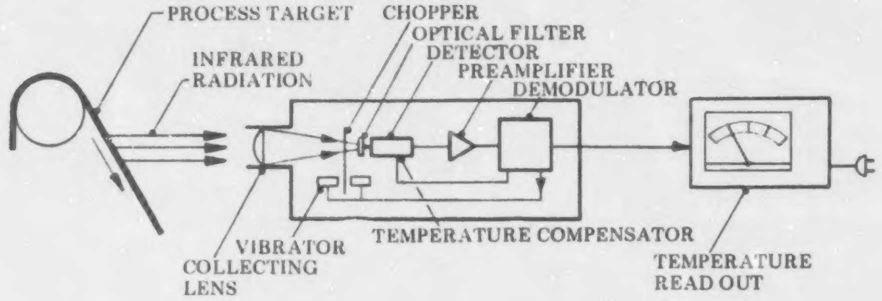

PROCESS TARGET
INFRARED RADIATION
CHOPPER
OPTICAL FILTER
DETECTOR
PREAMPLIFIER
DEMODULATOR
VIBRATOR
COLLECTING LENS
TEMPERATURE COMPENSATOR
TEMPERATURE READ OUT

FIG. C-15. Infrared thermometer schematic. Wahl Model HSM500 (Ref. 21).

Instrumental Analysis of Water Pollution Control by Mancy (Ref. 22), and the chapter, "Measurement of Ocean-Surface Temperatures," by Wormser in Fundamentals of Infrared Technology (Ref. 25).

d. Temperature-Depth Profile Recorders

Systems are available for monitoring water temperatures (and other parameters) as a function of water depth. For example, the block diagram in Figure C-16 shows an InterOcean system which can provide both water samples and water quality data at various depths. A somewhat simpler system is the InterOcean Model 550 Self Contained Recording Profiler which monitors temperature plus three other parameters (selected from pH, salinity, conductivity, dissolved oxygen, turbidity) as a function of depth. Two parameters are measured while the sensor system is being lowered; the other two while it is being raised. The data are recorded as a function of depth on chart paper which is enclosed inside the housing. See the Instrument Note for additional information.

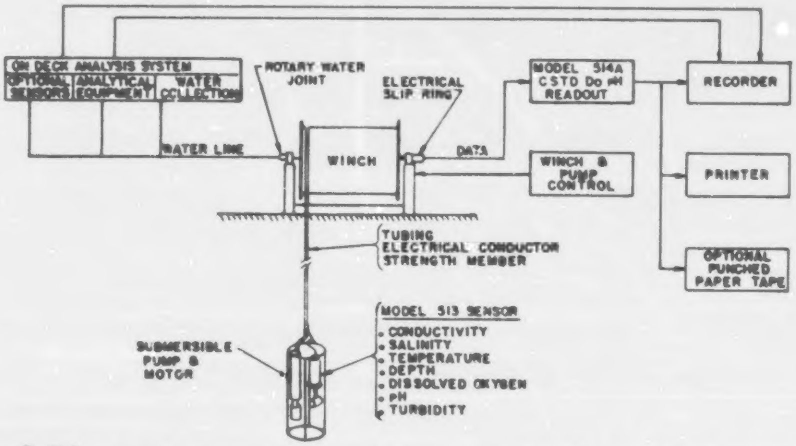
D. SUMMARY AND CONCLUSIONS

Techniques for measuring the temperature of water appear adequate for most purposes. Monitoring water temperature may be carried out manually or automatically, and from remote distances. Instrumentation is available to obtain temperature profiles as a function of depth. The various options are summarized in the Table of Instrumentation which is given in the next section.

Attention should be directed to proper calibration of the technique selected for measurement of water temperature. The calibration procedure should center around a reliable temperature standard.

E. ACKNOWLEDGMENT

Thanks are given to C.C. Coutant, Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN, and to H.H. Plumb, Thermometry Laboratory, Heat Division, National Bureau of Standards, Washington, DC, for their comments.


ON DECK ANALYSIS SYSTEM
OPTIONAL SENSORS
ANALYTICAL EQUIPMENT
WATER COLLECTION
ROTARY WATER JOINT
ELECTRICAL SLIP RING
MODEL 514A CSTD Do pH READOUT
RECORDER
WATER LINE
WINCH
DATA
WINCH & PUMP CONTROL
PRINTER
TUBING
ELECTRICAL CONDUCTOR
STRENGTH MEMBER
OPTIONAL PUNCHED PAPER TAPE
MODEL 513 SENSOR
CONDUCTIVITY
SALINITY
TEMPERATURE
DEPTH
DISSOLVED OXYGEN
pH
TURBIDITY
SUBMERSIBLE PUMP & MOTOR

C-16 ***Block diagram of the InterOcean Ocean Sampling and Environmental Analysis System.***

TABLE OF SELECTED INSTRUMENTATION FOR
MONITORING THE TEMPERATURE OF WATER

Principle of Operation	Multiparameter Capability	Accuracy	Cost $	Remarks
Liquid-in-Glass Thermometer				
Arthur H. Thomas, 9310	None	±0.5 to 1°C tolerance	$4.95-7.10	Inexpensive and easy to use, but fragile.
Metal Resistance Thermometers				
Enviro Control, Model 1009	None	±1% of full scale		Pt wire sensing element. Cable lengths up to 610 m (2000 feet) available.
InterOcean, Model 550	pH, Salinity, Dissolved Oxygen, Conductivity, Turbidity, Depth			Pt wire sensing element available as option to thermistor, if increased accuracy and response are desired.
Ionics, Inc., Series 1600	pH, Dissolved Oxygen, ORP, Turbidity, Conductivity, Dissolved Chlorides			Pt wire sensing element. Water is pumped to sensor module.
Omega Engineering, Model PR11	None	±0.01°C	$39-45	Sensing element is Pt wire wound upon ceramic core. For 1/4" diameter sheath, response time to 63% of a step change in temperature is <5 sec.
Thermistor Resistance Thermometers				
Beckman Enviroline, Model EV6	Conductivity	2°C	$ 168	<1 sec response. Battery powered.
InterOcean, Model 550	(See Metal Resistance Thermometers)	±0.02°C	$9750	60 millisec time constant. To 6000 meter depth.
Omega Engineering, H-91	None	±0.2°C	$29.50	Closed end stainless steel tube, with thermistor mounted in tip.
Yellow Springs, Model 42	None	0.5°C	$ 165	Battery powered.
Thermocouple				
Doric Scientific, Model DS-520-T3-M	None	2°, or ±0.5%	$ 395	Direct numerical display of temperature reading (Nixie).
Omega Engineering, Model DS-500	None	0.25%	$ 595	Direct numerical display of temperature reading (Nixie).
Thermo Electric, Model DTI/611	None	0.1%	$ 895	Direct numerical display of temperature reading (Nixie).
Infrared Thermometer				
Wahl Model 150A	None	0.5°C	$2995	Surface temperature. Non-contact.

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H2O-PHY
Field or Laboratory: TEM
Doric 1
June 1973

Doric Scientific Corporation Digital Thermocouple Indicator

Model DS-520-T3-M

615
THERMOCOUPLE INDICATOR
DS-520

Class	Continuous - Sensor
Categories of Water	Fresh, Saline, and Waste
Principle of Operation	The millivolt difference between the "hot" water temperature measuring junction and the "cold" reference junction of the thermocouple type being used is digitized, and electronically converted to the corresponding temperature reading by means of a read-only memory (ROM). The ROM stores the look-up tables (programmed using data from the National Bureau of Standards) by which the digitized millivolt data are converted to temperature readings. The temperature is displayed numerically on the front panel of the instrument. The reference junction potential is provided by a zener diode, which mimics the 0°C temperature of the ice point of a standard water-ice mixture.
Minimum Detectable Sensitivity	1°C
Range	Depends on thermocouple materials. 0°C to 100°C covered by thermocouples.
Interferences	None
Multiparameter Capability	None
Sampling	Method: Place sensor in water Volume: Maximum Number of Sample Sources: 12

Performance

Accuracy: ±0.5% of reading, or ±2°, whichever is larger
Reproducibility: 1°C resolution and repeatability
Linearity: Included in accuracy statement
Noise: Included in accuracy statement
Lag Time:)
Rise Time:) Included in sample rate interval
Fall Time:)
Retention Time: N/A
Zero Drift: Automatic zero
Span Drift: 2°F/yr maximum with base metal thermocouple

Operation

Ambient Temperature Range: 10°C to 40°C (50°F to 104°F). Operates at reduced accuracy over range 0°C to 50°C.
Temperature Compensation: Cold junction compensation: automatic from 0°C to 50°C
Relative Humidity Range: 10 to 90%
Procedure: Insert thermocouple sensor into water sample, and read. Sample rate is 3 to 4 readings per second. Instrument should warm up about 30 minutes prior to reading.
Unattended Period: Operator attention not required.
Maintenance: No periodic maintenance requirements.

Requirements

Power: 105 to 125 Vac, 50 to 400 Hz, 17 Watts, maximum. For portable operation, nickel-cadmium batteries can provide 6 hours of continuous operation.
Weight: 6.8 kg (15 lb)
Dimensions: "A" Chassis: 37.46 L x 7.62 H x 21.59 W cm
(14-3/4" L x 3" H x 8-1/2" W)
"B" Chassis: 37.46 L x 11.43 H x 21.59 W cm
(14-3/4" L x 4-1/2" H x 8-1/2" W

Features

Output: Inline visual Nixie display. Can be interfaced to digital, punch, or computer.
Training:

Options:

S6P	Isolated BCD Output (Factory Installed) positive true	$ 95
220V/50 Hz	Power for Export Operation	25
ISC-12	Integral 12-Point Selector Switch	250
ESC-12	External 12-Point Selector Switch (Uses "A" Chassis)	175
ESC-24	External 24-Point Selector Switch (Uses "A" Chassis)	305
IL	Interlocking switches per 12-point switchboard (Switches do not interlock from board to board)	N/C
ID	Electrical Switch Point Identification per 12 Channels (Not available when DB option is used)	75
DB	Display Blanking (if more than one pushbutton is inadvertently engaged)	
	Each 12-channel switchboard } Not available when ID option is used	75
	Each Instrument } Not available when ID option is used	100
BP	Rechargeable Battery Pack (Mounts in "A" Chassis)	500
DC	Operation from External 12 VDC Source (Mounts in "A" Chassis)	195
W	Rack Adapter for "B" Chassis (single or dual 5-1/2" x 19")	75
W1	Panel Mounting Hardware for "B" Chassis	25
W3	Panel Mounting Hardware for "A" Chassis	25
W4	Rack Adapter for "A" Chassis (single or dual 3-1/2" x 19")	45

References

1. Above information obtained from Manufacturer's brochure, Bulletin 520-3-73-5K, dated 1972, and Bulletin T3-73-5K, entitled "Thermocouple Thermometry".
2. Manufacturer's letter, dated June 21, 1973.

Cost

DS-520-T3-M Digital T/C Indicator with Built-in Reference Junction $395

Remarks

Circuitry is all silicon, solid state. Uses medium scale integration (MSI) and large scale integration (LSI) integrated circuits. Temperature display is 1.27 cm (0.5") numeral height Nixie indicators.

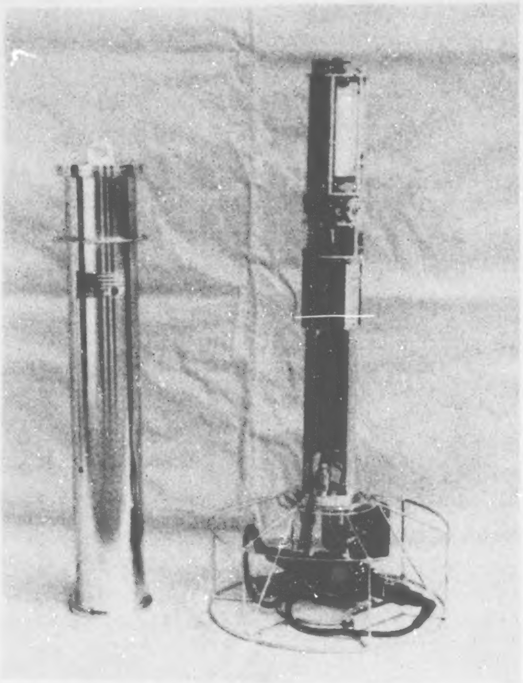
Address

Doric Scientific Corporation
7601 Convoy Court
San Diego, CA 92111
Attn: Mr. R.E. Lagrand, Sales Manager
(714) 277-8421

Doric Scientific S.A.
Dreve du Caporal 33
11 Brussels, Belgium
74.67.12

InterOcean CSTD Self Contained Graphic Recording Profiler

Model 550



Class	Continuous - sensor
Categories of Water	Fresh, Saline, and Waste
Principle of Operation	The Model 550 is a self-contained multiparameter system. Four parameters (chosen from: temperature, pH, salinity, conductivity, dissolved oxygen, turbidity) are measured. Two are measured while the sensor system is being lowered; the other two while it is being raised. Data are recorded as a function of depth on pressure sensitive chart paper, which is enclosed inside the housing. As an alternative, the instrument may be supplied with an internal, digital magnetic tape cassette recorder to record conductivity, salinity, temperature, depth, pH, dissolved oxygen, turbidity, current speed, direction. The instrument may be used to obtain profiles or it may be installed to collect long term, round-the-clock data.
Minimum Detectable Sensitivity	
Range	-5 to +45°C
Interferences	For temperature, none.
Multiparameter Capability	Conductivity: 0-65 ±0.02 mmhos/cm standard 0-6.5 ±0.002 mmhos/cm optional Salinity: 0-40 ±0.02 ppt; expanded ranges available Depth: 0-100, 300, 500, 1000, 2000, 3000 and 6000 m available; ±0.25% FS Dissolved Oxygen: 0-20 ppm ±1% pH: 2-12 pH ±1% Turbidity: 0-200 JTU 1% resolution 0-100% transmission 1% resolution

Sampling

Method: Continuous
Volume: N/A
Maximum Temperature Input:
Collection Efficiency:
Maximum Number of Sample Sources: One

Performance

Accuracy: ±0.02°C
Reproducibility:
Linearity:
Noise:
Lag Time:
Rise Time: 60 millisec time constant
Retention Time:
Fall Time:
Zero Drift:
Span Drift:

Operation

Ambient Temperature Range: -10°C to +65°C
Temperature Compensation: Automatic
Relative Humidity Range: N/A
Calibration:
Procedure: The sensor package is lowered into the water to the desired depth, then raised back. Measurement and recording are automatic.
Unattended Period: 90 days
Maintenance: Replace batteries, as required. Clean housing and sensors.

Requirements

Power: Self-contained rechargeable batteries
Weight: 50 Kg (110 lb)
Dimensions: 120.7 cm H x 48.3 cm dia (47-1/2" H x 19" dia)

Features

Output: Enclosed recorder, chart paper - 16.5 cm x 24.1 cm (6-1/2" x 9-1/2")
Training: Contact manufacturer.
Options: Selection of 4 of 6 sensors (7 sensors, with magnetic tape option).
Depth ranges: 0-100, 300, 500, 1000, 2000, and 6000 m; ±0.25% full scale accuracy

References

1) Manufacturer's brochure "Self Contained Graphic Recording Profiler, Model 550", undated.
2) Manufacturer's summary catalog, 1973.
3) Manufacturer's letter, dated June 25, 1973.

Cost

Model 550 $9,750 for basic unit.

Remarks

Temperature sensor is a linearized thermistor, with a stainless steel shroud. An optional platinum resistance thermometer is available for increased accuracy and response.

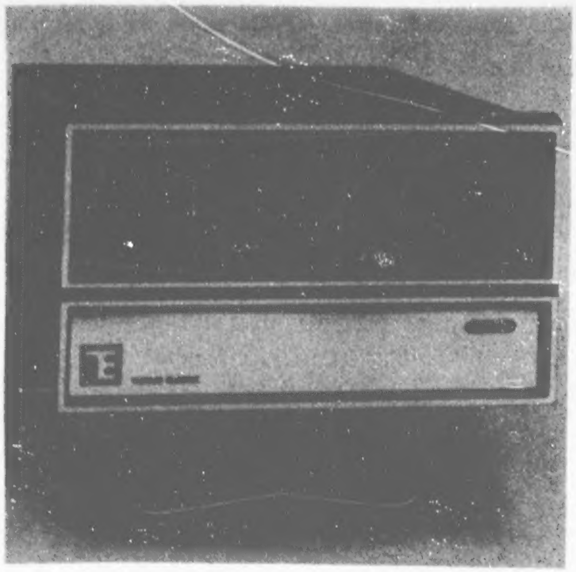
Address

InterOcean Systems, Inc.
3510 Kurtz St.
San Diego, CA 92110
Attn: Mr. Joel J. Sigalove
(714) 299-4500 Telex: 695082

H20-PHY
Laboratory: TEM
Thermo Electric 1
June 1973

Digital Temperature Indicator

Thermo Electric Model DTI/611



Class	Continuous - sensor
Categories of Water	Fresh, Saline, Waste
Principle of Operation	The change in voltage of a thermocouple sensor is linearized, and converted to digital readout for numerical display.
Minimum Detectable Sensitivity	±4 to 10 μV, depending on range.
Range	Depends on thermocouple used. Covers water temperature ranges.
Interferences	None
Multiparameter Capability	None
Sampling	Method: Place thermocouple probe in water Volume: N/A Maximum Temperature Input: Collection Efficiency: 1 to 4 samples per second Maximum Number of Sample Sources: One
Performance	Accuracy: 0.1% Reproducibility: ±1°C repeatability Resolution: 0.1°C Linearity: Noise: <4 μV Lag Time: Depends on sample time. Rise Time: 2 sec response time Retention Time: One sample period Fall Time: Equals rise time Zero Drift: ±0.015% full scale for 60 days, ±0.03% for 6 months stability Span Drift: 0.015% full scale over 90 days.

Operation

Ambient Temperature Range: 4° to 49°C (40° to 120°F)
Temperature Compensation: Automatic
Relative Humidity Range: Information not available
Calibration:
Procedure: Thermocouple sensor is placed in the water sample, and the temperature is recorded.
Unattended Period:
Maintenance: Calibration check every 90 days.

Requirements

Power: 117 to 230 Vac ±10%, 50 to 60 Hz, 30 Watts
Weight: 5.6 kg (12.5 lb)
Dimensions: 12.19 cm × 20.78 cm × 32.38 cm (4.80" × 8.18" × 12.75")

Features

Output: BCD (TTL, RTL, DTL), 0 to 10 V linear analog
Training: None required
Options: Multipoint switching

References

Manufacturer's brochure, "DTI/611 Digital Temperature Indicator," 1972
Manufacturer's communication, dated June 25, 1973

Cost

$895

Remarks

A range of industrial thermocouples are available from the manufacturer. See manufacturer's brochure "Industrial Thermocouples," Edition 3, 1967.

Address

Thermo Electric
Saddle Brook, NJ 07662
(201) 843-5800 Teletype 710-990-5108

H2O-PHY
Field: TEM
Yellow Springs 1
June 1973

Tele-Thermometer

YSI Model 42

YSI MODEL 42SC
TELE-THERMOMETER
°C
PROBE

Class	Continuous - sensor
Categories of Water	Fresh, Saline, Waste
Principle of Operation	Water temperature changes cause a change in the resistivity of a thermistor sensor. The thermistor constitutes one arm of a Wheatstone Bridge, so that the resistance change causes the bridge to be unbalanced so that a current flows. The bridge unbalance is related to the temperature by calibration data, and the temperature is displayed in analog fashion on a meter.
Range	-80° to +40°C (-20° to +80°F) or -40° to +150°C (-40° to 302°F)
Interferences	None
Multiparameter Capability	None
Sampling	Method: Thermistor sensor is placed in water being monitored. Volume: NA Maximum Temperature Input: Collection Efficiency: NA Maximum Number of Sample Sources: One

Performance

Accuracy: 0.5°C
Reproducibility: 0.2°C
Linearity:
Noise:
Lag Time: NA
Rise Time: NA
Retention Time: NA
Fall Time: NA
Zero Drift:
Span Drift:

Operation

Ambient Temperature Range: -40° to +50°C (-40° to +120°F)
Temperature Compensation: Yes
Relative Humidity Range: NA
Calibration:
Procedure:
Unattended Period: NA
Maintenance: Periodic battery replacement

Requirements

Power: Models 42 SC, SF, SE, two 6.75 volt mercury batteries. Model SL has three 6.75 volt mercury batteries.
Weight: 1.36 kg (3 lb)
Dimensions: 16.5 cm H x 11.5 cm D x 16.5 cm W (6-1/2" x 4-1/2" x 6-1/2")

Features

Output: 0 to 120 mV recorder output
Training: None
Options: YSI Model 80A single channel recorder, $450.00
YSI Model 81A dual channel recorder, $695.00
Broad range of thermistor probes are available.

References

1) Manufacturer's brochure, "YSI Temperature Instruments", CTC-April, 1971
2) Manufacturer's brochure, "YSI Thermistor Probes", PRB-April, 1970
3) Manufacturer's letter, received July 5, 1973

Cost

YSI Model 42	$165
Manufactured to order	$180
YSI 4003 Carrying Case	$ 12

Remarks

Temperature probes for use with the Model 42 are available in a variety of configurations at prices from $15 to $90, approximately.

Address

Yellow Springs Instrument Co.
P.O. Box 279
Yellow Springs, OH 45387
Attn: Dick Horn
(513) 767-7241

E. CONTENTS FOR TURBIDITY MONITORING INSTRUMENTATION

	Mnemonic
A. Introduction	H2O-PHY Introduction: TUR
1. Characteristics of Turbidity	
2. Sources and Control of Turbidity	
3. Deleterious Effects of Turbidity in Water	
4. Water Quality Standards for Turbidity	
5. Sampling for Turbidity Measurement	
6. Calibration of Instrumentation	
B. Methods for Turbidity Measurement	H2O-PHY Methods: TUR
1. Light Scattering	
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A. INTRODUCTION

Turbidity is a state of lacking in clarity or translucence. In water quality criteria, it is an expression of the optical property of a sample which causes light to be scattered and absorbed rather than transmitted in straight lines through the sample. Turbidity in water is due to the presence of suspended particulate matter, such as clay or silt, finely divided organic and inorganic matter, plankton, suspended oils, bacteria or other microscopic organisms. It is difficult indeed to obtain water which does not have a measurable amount of turbidity. Even fresh rain water usually has some turbidity due to the leaching out of dust and smog constituents by the passage of raindrops through the atmosphere.

While a small amount of turbidity is quite permissible in water for ordinary usage, including even drinking, the level at which this type of contamination can be tolerated is quite low. Furthermore, turbidity above a certain level may be quite harmful. Therefore, it has been necessary to develop means for its measurement and units in which to express turbidity concentrations. These topics are discussed further under the appropriate sections.

Measurements of turbidity in common use do not correlate with the weight concentration of suspended matter because the size, shape and refractive index of particulates are important from a scattering standpoint, but bear little direct relationship to concentration and specific gravity. This is because turbidity in treated waters is measured primarily by methods which record the intensity of light scattered in the forward or side direction by the water sample. Some turbidimeters read and record data in terms of % transmission, and monitor any decrease in the intensity of the incident light. The decrease in intensity can be caused by both absorption or scattering of the radiation from the light source. A very small amount of light is scattered by a suspension of low turbidity, hence the incident and transmitted light beams have essentially the same intensity. It is difficult to distinguish between these two nearly identical intensities unless very long light paths are used, therefore such instruments are not useful at low turbidities.

Turbidity in its classical sense refers to the capacity to obscure. Early measurements detected obscuration of a platinum wire or an enameled plate. The obscuring effect of turbid suspensions cannot be measured directly (e.g., the Secchi disc method) at low turbidities without unacceptably long path lengths. As a result modern instruments have relied on light scattering caused by turbid suspensions.

An immediate problem occurs since scattering at various angles to the incident light beam varies according to the wavelength of the incident light and the specific nature of the particles. A substantial case has been made for the measurement of scattered light at low angles (15° to the incident light beam). Satisfactory instruments for the purpose have cost too much for widespread use, so the simpler instruments employing wide angle scattering have captured the market and definitions have been modified to fit. The choice is not clear-cut because particle sizes less than 0.5 µm diameter yield turbidities (haze) best measured by wide angle scattering. Wide angle instruments are one-half or less the cost of low angle instruments and their present popularity does not appear threatened.

Since most applications of turbidity measurements need to be consistent only for in-house comparisons and not for data from different sources, some sacrifice in rigor of definition has been acceptable. More stringent water quality standards of national application may alter this attitude. Of all tests of water quality, turbidity testing has long been one of the most common, and most unsatisfactory tests.

1. Characteristics of Turbidity

Substances normally producing turbidity consist largely of clay minerals and microscopic organisms. These substances occur in widely varying sizes ranging from those large enough to settle to those small enough to remain suspended for very long times (Ref. 1, p. 69-70). Removal of turbidity-causing constituents to AWWA recommended levels for high-quality finished water (0.1 unit) by coagulation with alum still leaves an enormous number of particles. These represent either uncoagulated clay particles or fragments of coagulant floc which have passed through the filters. It can be calculated tha each liter of treated high-quality water will contain about 2×10^8 particles of insoluble alum coagulant, assuming a suspended solids content of 0.1 mg/l and sphere 1 µm in diameter with specific gravity of 1.01 (Ref. 1, p. 71).

As noted, particles causing turbidity in raw waters are often inorganic, and can range from about 0.2 μm to 5.0 μm or larger. The fraction exceeding 1 μm in diameter is generally referred to as silt and will settle out on standing. The smaller particles are classified as colloidal and can remain suspended for a very long time.

Colloids are distinguished by a high ratio of surface area to mass; they may also carry an electrostatic charge. Because of this charge, colloidal particles can attract ions of opposite charge to the colloid surface so that the chemistry of the water system is altered. Most turbidity is due to particles occuring in the upper size range of true colloids (Ref. 1, p. 87).

Turbidity is discussed further in Water Quality and Treatment, A Handbook of Public Water Supplies (Ref. 1); some effects of turbidity and industrial and municipal specifications appear in Water Quality Criteria (Ref. 2).

2. Sources and Control of Turbidity

Contaminants contributing to turbidity in water include those from land erosion, decay of organic vegetation, clay minerals, and microscopic organisms. Sources of turbidity directly traceable to man's activities include silt from farms, road building and housing development projects, mining operations, unprotected road cuts (Ref. 2, p. 47), and sewage or sewage plant effluents. Natural turbidity varies widely throughout the United States.

Turbidity in water is removed primarily by a combination of coagulation, sedimentation and filtration. The method using alum as the coagulant has been used since ancient times, perhaps as far back as 2000 B.C., to purify water. It remains as the most widely used today, but iron salts and polyelectrolytes are also widely used. The polyelectrolytes in particular are of increasing interest as they greatly reduce the problem of sludge disposal. Other coagulants have included seeds, beans, macerated laurel, pounded barley, and chalk. Turbidities of treated water generally fall in the 0 to 5 Jackson Turbidity Units (JTU) range. (Ref. 3, p. 349). See Section 6 for definition of JTU.

Removal of turbidity with alum as an added coagulant requires careful attention to such factors as pH, temperature, and other constituents in the water. The subject is treated in detail in Water Quality and Treatment, A Handbook of Public Water Supplies (Ref. 1).

3. Deleterious Effects of Turbidity in Water

> The presence of suspended material such as clay, silt, finely divided organic material, and plankton contributes to the cloudiness or turbidity of water. Turbidity in excess of 5 units is easily detectable in a glass of water and is usually objectionable for aesthetic reasons. Clay or other suspended particles may not adversely affect health, but water containing such particles may require treatment to make it suitable for certain uses. Following a rainfall, variations in the ground water turbidity may be considered an indication of surface pollution. (Ref. 2, p. 125).

Excessive turbidity reduces light penetration into the water and, therefore, reduces photosynthesis by phytoplankton organisms, attached algae, and submersed vegetation. However, it may sometimes be desirable to inhibit their growth by adding turbidity-producing material to the water.

> Silt and sediment are particularly damaging to gravel and rubble-type bottoms. The sediment fills the interstices between gravel and stones, thereby eliminating the spawning grounds of fish and the habitat of many aquatic insects and other invertebrate animals such as mollusks, crayfish, fresh water shrimp, etc....Fish productivity is ultimately dependent upon plant life and a good bottom fauna. There can be little of either above 200 JTU if that turbidity is maintained continuously. (Ref. 2, p. 46-47)

Poor operation and loss of exchange capatigy in ion-exchange columns used to soften water can be caused by organic and/or inorganic turbidity. The particles can interfere by mechanically blocking the surface of the ion-exchange beads.

Additional discussion on deleterious effects of turbidity may be found in Water Quality Criteria (Ref. 2), and Water Quality and Treatment (Ref. 1).

4. Water Quality Standards for Turbidity

The U.S. Public Health Service suggested limit is 5 units for turbidity in drinking water. A turbidity limit of 0.1 unit has been recommended by the American Water Works Association Task Group 225M for high-quality finished water

(Ref. 1, p. 70). Standards related to specific industries such as baking, brewing, ice making may be found in Water Quality Criteria (Ref.2). Turbidity is one of the four General Physical Analyses required for domestic and water supplies quality and monitoring by the California Department of Public Health (Ref. 4).

5. Sampling for Turbidity Measurement

Samples of water intended for turbidity measurements should not be held longer than 7 days and according to the EPA method (Ref. 5, p. 4) do not have an added preservative. Turbidity may change on standing (Ref. 3, p. 35) so that, if possible, the sample should be analyzed on-site, or at least on the day the sample is taken. According to Standard Methods (Ref. 3, p. 350), samples may be stored in the dark up to 24 hr, or even longer, if each liter of sample is treated with 1 g of mercuric chloride. Prolonged storage before measurement is not recommended. All samples should be vigorously shaken before examination, with care to allow bubbles to disappear before measurement.

6. Calibration of Instrumentation

Calibration of turbidimeters is usually made with a silicate or formazin suspension. The stock suspension of formazin is prepared from:

1. Solution 1:
   1.000 g hydrazine sulfate per 100 ml distilled water, mixed, and diluted in a volumetric flask.

2. Solution 2:
   10.00 g hexamethylenetetramine per 100 ml distilled water, mixed, and diluted in a volumetric flask.

A suspension with a turbidity of 400 units is prepared from the stock solutions by pipetting into a 100 ml volumetric flask: 5.0 ml of solution 1 and 5.0 ml of solution 2. The resultant solution is mixed and allowed to stand 24 hr at 25 ± 3°C then diluted to mark and mixed (Ref. 3, p. 351). Dilution of 10.00 ml of this stock suspension to 100 ml with turbidity-free water yields a suspension which is defined as 40 units (JTU, or Jackson Turbidity Units). It may be diluted as required to prepare more dilute turbidity standards (Ref. 6, p. 157) which are stable for about a week.

The analytical instrument must be calibrated before use according to the manufacturer's operating instructions over the range of interest. Reliable results will not be obtained unless the calibration procedure is carried out at the time samples are run, partly because of instrument drift. Turbidity readings are recorded in Jackson Turbidity Units (JTU), turbidity units, or units. (Sometimes results are reported as ppm (Ref. 7)). A clear sample would have 0 JTU turbidity; the upper limit of turbidity is usually 1000 JTU.

Turbidity is calculated from the calibration curve data using the equation (Ref. 6, p. 157):

$$\text{JTU} = \text{Observed turbidity} \times \frac{\text{final dilution volume}}{\text{original sample volume}}$$

From the above equation it is obvious that turbidity varies linearly with the concentration of suspended material. Readings are recorded to the nearest unit in terms of the following table (Standard Methods, Ref. 3, p. 352) for a nephelometric turbidimeter:

Turbidity Range in Units	Recorded to the Nearest
0-1.0	0.05
1-10	0.1
10-40	1
40-100	5
100-400	10
400-1000	50
>1000	100

For comparison of water treatment efficiencies, it may be desirable to estimate turbidity more closely than is specified in the above tabulation. However, the uncertainties and discrepencies in turbidity measurements make it unlikely that two or more laboratories will duplicate results on the same sample more closely than specified in the table (Ref. 3, p. 353).

Silicates such as kaolin composed of amorphous hydrous aluminum silicates with colloidal structure can be used as calibration standards in forward-scattering methods (Ref. 3, p. 354). However, stable, reproducible standards with particle diameters in the 1 to 10 μm range are not currently available (Ref. 7).

Additional discussion on calibration is found in Standard Methods for the Examination of Water and Wastewater (Ref. 3) and Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases (Ref. 6).

B. METHODS FOR TURBIDITY MEASUREMENT

Methods used to monitor turbidity in water include both light scattering and light transmission measurements. A colored sample can attenuate a light beam affecting both transmission and scattering measurements. The relative magnitudes of scattering and transmission in a single water sample may be estimated by: (1) measuring % transmission, (2) filtering the sample, and (3) measuring % transmission in the filtered water sample. The difference in % transmission between the unfiltered and filtered sample is then taken as a measure of the turbidity.

1. Light Scattering

There is very little tendency for a true solution ("particle" diameter < 10^{-7} cm) to scatter light. However, for colloidal dispersions (particle diameters in the range 10^{-4} to 10^{-6} cm), a beam of light has its path illuminated because the light is scattered. The intensity of the scattered light depends on such factors as intensity of incident light, the difference between the refractive indices of the particles and water (or other medium); particle size; number of particles per volume; wavelength of the incident light; and, angle at which the scattered light is measured.

In the absence of absorption, particles in the colloidal size range scatter light of lower wavelength (ultraviolet to blue range) more intensely than radiation of higher wavelength. The scattered intensity falls off as the negative fourth (-4) power of the wavelength of the incident light -- a relation first discovered by Rayleigh. See Figure B-1.

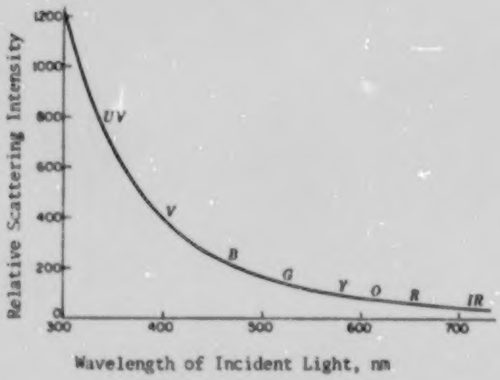


FIGURE B-1. Intensity of scattering vs wavelength according to Rayleigh's law.

When particles are small by comparison with the wavelength of the incident light, scattering occurs in an angular pattern. See Figure B-2 (Ref. 8). The intensity of the light scattered in any direction is proportional to the distance from the origin of the curve in that direction. The shape of Figure B-2 is

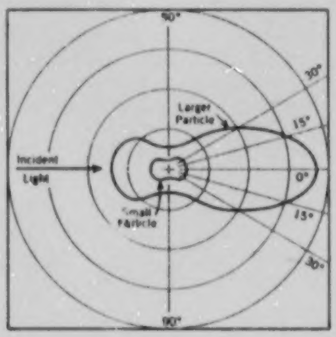


FIGURE B-2. Scattering intensities from small and large particles as a function of angle (Ref. 8).

The larger particle scatters about 8 times as much light at 15° as it does at 90°. Very large particles typically found in treated water scatter more than 100 times as much light at 15° as at 90°.

> "due to complete polarization of the unpolarized incident light scattered at 90° and partial polarization at angles other than 0° and 180°. Note that for relatively small particles, scatter is symmetric in forward and backward directions about 90°, with the scattered intensity at 0° and 180° twice the scattered intensity at 90°.
>
> "As particle size increases, scattered waves from different parts of the same particle begin to exhibit mutual interference, as shown in Fig. [B-3]. Rays scattered in forward directions tend to be in phase and additive whereas those scattered in backward directions tend to be out of phase or destructive. The net effect is a greater measured intensity of light scattered in the forward directions, as shown in the large curve of Fig. [B-2]." (Ref. 8)

In turbidimeters, light scattering is measured either in the forward (low-angle, 15°) direction, or from the side (90 ± 30°) direction from that of the incident light. An advantage of the on-line forward direction measurement includes a higher scattering intensity than side-scattering. Disadvantages of in-line forward-scattering include greater susceptibility to stray light and higher cost of using instrumental readout as compared to side-scattering measurements. Side-scattering instrument advantages include a less critical angle of measurement and possible higher sensitivity in measuring low turbidity because of the dark background representing zero concentration as compared to full illumination at zero concentration in the forward-scattering method.

1.1 Forward-Scattering Instruments

The Jackson candle turbidimeter has been used as the standard method for turbidity measurements. See Figure B-4. The method is based on the length of the light path through the turbid suspension which just causes the image of the flame of a standard candle to become indistinguishable when viewed against the general background illumination. In this method, attention must be given to factors including proper placement of the candle and glass tube, absence of air drafts, frequent trimming of the charred portion of the wick, and candle burning time. The candle is composed of beeswax and spermaceti, and is designed to burn between 114 to 126 grains per hour (1 grain is 0.0648 g). The Jackson candle

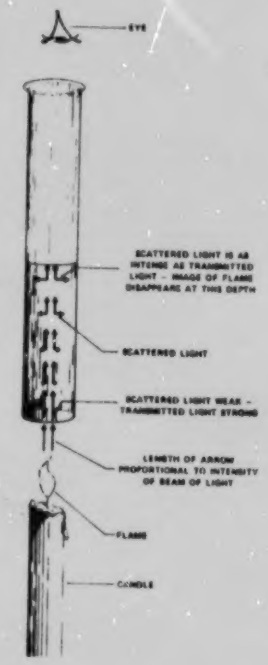

EYE
SCATTERED LIGHT IS AS INTENSE AS TRANSMITTED LIGHT - IMAGE OF FLAME DISAPPEARS AT THIS DEPTH
SCATTERED LIGHT
SCATTERED LIGHT WEAK - TRANSMITTED LIGHT STRONG
LENGTH OF ARROW PROPORTIONAL TO INTENSITY OF BEAM OF LIGHT
FLAME
CANDLE

FIGURE B-4. Schematic of Jackson Candle Turbidimeter (Ref. 9).

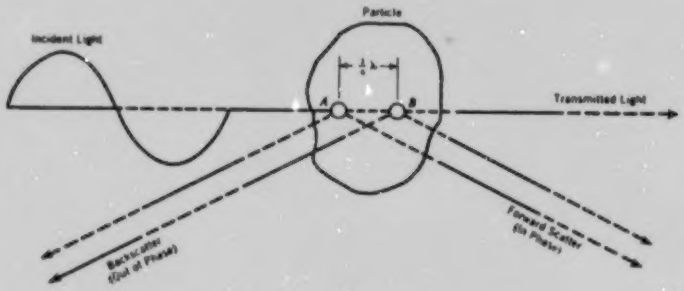

Particle
Incident Light
$\frac{1}{4}\lambda$
A
B
Transmitted Light
Backscatter (Out of Phase)
Forward Scatter (In Phase)

FIGURE B-3. Interference of light scattered by a large particle (Ref. 8).

Positive and negative phases of the light waves are represented by solid and dashed lines, respectively. Waves scattered in the forward direction from sites A and B within the particle have travelled essentially the same distance in a given time and remain in phase giving a high intensity of scattered light. Light scattered in a backward direction from point B has travelled 1/4 λ farther than point A before being scattered and must return approximately 1/4 λ to interfere with light scattered from point A. Backscattered waves for this example are almost exactly out of phase giving a low intensity of scattered light in the direction shown.

turbidimeter is limited to turbidity values between 25-1000 JTU (Ref. 3). Water samples with turbidities exceeding 1000 JTU are diluted so that they will fall in the 25 to 1000 range. Samples measuring less than 25 units must be run by other methods such as nephelometric, or comparison with bottle standards.

Measurements using the Jackson Candle Turbidimeter are made by slowly pouring the sample into a graduated glass tube while visually observing the image of the candle flame from the open top of the tube. The sample is poured into the tube until the image disappears into a uniform glow. The turbidity is less the higher the column of water sample in the graduated glass tube before extinction. For example, calibration data in Standard Methods (Ref. 3, p. 353) show 1,000 turbidity units corresponds to 2.3 cm; 25 units to 72.9 cm.

Besides not being applicable for turbidities below 25 units, the Jackson Candle is not capable of measuring black particles. This is because light absorption is much greater than any scattering effects: The field of view becomes dark before enough sample is poured into the tube to reach extinction of the image.

The candle flame emits light at the long (yellow-red) wavelength end of the visible spectrum so that very fine particles do not produce a flame extinction using a Jackson Turbidimeter. These fine particles can be measured by instruments using an incandescent lamp as the light source (Ref. 9).

Turbidity also can be estimated in the range of 5-100 J.T.U's by comparing a sample of unknown turbidity against a series of standard turbidity suspensions, all in identical glass bottles (Ref. 3). Artificial lighting must come from either above or below the bottles so that no direct light reaches the eye. The suspensions are compared by observing the same newsprint or ruled lines through the sides of the bottles. The turbidity of the unknown is considered to be the value of the standard which produces the visual effect most closely approximating that of the sample.

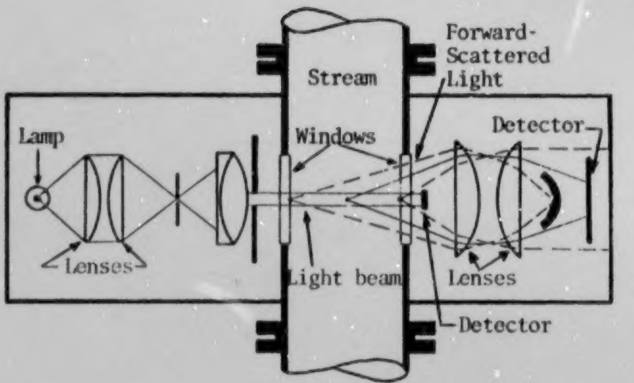


FIGURE B-5. Optical schematic for an in-line forward-scatter turbidimeter.

The forward-scattering turbidity instruments manufactured by Monitor Technology, record the ratio of light scattered at low angles (~15°) to that of light transmitted through the sample. See Figure B-5. Light from the source is directed through the sample to a direct beam detector phototube, and is taken as a measure of unscattered light. Light scattered in the forward direction by particles, passes to each side of the direct beam detector onto the scattered beam detector. The ratio of the two signals is then recorded. Instruments using this approach would appear to minimize the effects of bubbles and changes in intensity due to light absorption by a colored sample rather than light scattering. They are reported to provide linearity of the output ratio with turbidity to the low ppb ranges (Ref. 7). A disadvantage is their relatively high cost (about 2 to 3 times that of side-scattering instruments).

1.2 Side-Scattering Instruments

Modern instrumental methods used to measure turbidity in water include the nephelometric method which measures the intensity of light scattered at side angles to the incident light. For practical applications, the turbidimeter should measure from 0 to 40 units, and have a sensitivity sufficient to detect turbidity differences of 0.02 units or less in waters having turbidities less than 1 unit. The turbidimeter should be so designed that little stray light reaches the detector in the absence of turbidity, and should be free from significant drift after a short warmup period.

The Hach Model 2100 is representative of 90° nephelometers used to measure turbidity in water. A light beam from a tungsten lamp is passed through the sample and the intensity of the scattered light is measured using a photomultiplier tube in the detector portion of the instrument. See Figure B-6. Interferences in readings of true turbidity include air bubbles, large or coarse particles, and true (dissolved) color. Attention must also be given to good housekeeping practices in terms of keeping sample tubes cleaned and avoiding use of badly scratched tubes. Air bubbles and

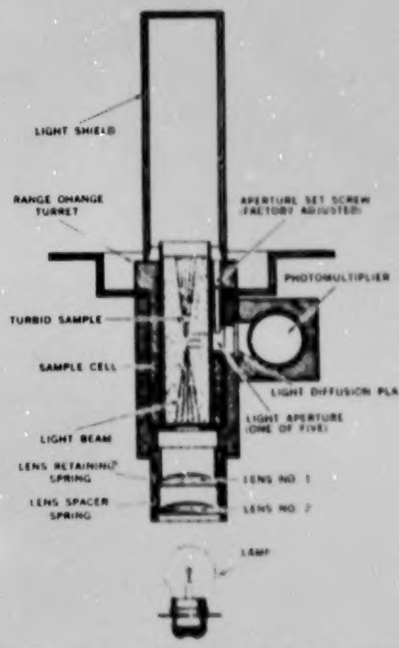


FIGURE B-6. Schematic of Hach Model 2100 nephelometer (Ref. 9).

coarse sediments will give high readings, and must be allowed to bubble out and settle out before measurement. Any dissolved color can absorb light; low results may be obtained unless corrected by filtering out the particles and remeasuring to determine intensity lost by absorption.

In the Hellige Model 8000 T, light rays from the source are deflected by a reflector to illuminate the turbid solution in the tube from the side. The light scattered upward by the suspended particles in the solution is seen through the ocular as the outer portion of the circular split fields shown in Figure B-7. Light rays from the bulb also pass through an adjustable precision slit and illuminate the reflector below the tube. They are deflected through the light filter, the circular aperture of the mirror and the turbid solution in the tube. When observed through the ocular, these light rays are seen as the center of the circular split fields shown in Figure B-7 I. The center of the field will appear lighter or darker then the outer portion depending upon the amount of light permitted through the adjustable slit. By revolving the graduated dial, it is possible to regulate the light until the two portions form one field of uniform intensity (Ref. 10). The manufacturer provides charts which relate dial readings to turbidity units. As a precaution, the user should calibrate the instrument using formazin or other approrpiate standards.

Differences in physical design of nephelometers can cause differences in measured values for turbidity even though the same suspension is used for calibration. To minimize such differences, the following design criteria should be observed (Standard Methods, Ref. 3, p. 351):

a) *Light source:* Tungsten lamp operated at not less than 85% of rated voltage nor more than rated voltage.

b) *Distance traversed by incident light and scattered light within the sample tube:* Total not to exceed 10 cm.

c) *Angle of light acceptance of the detector:* Centered at 90° to the incident light path and not to exceed ±30° from 90°.

d) *Maximum turbidity to be measured:* 40 units.

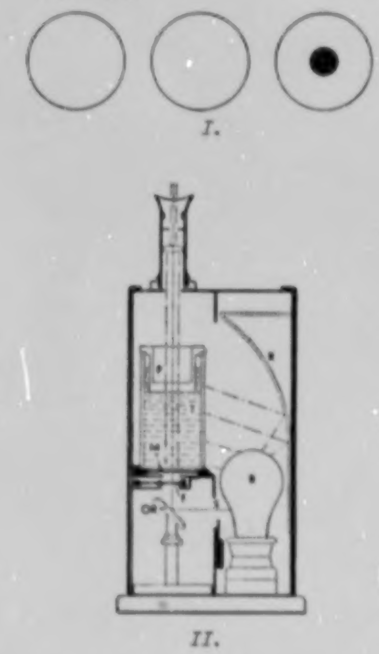


FIGURE B-7. Schematic of Hellige 8000 T (Ref. 10).

B = Opal glass bulb light source.
R = Reflector.
T = Sample tube.
S = Slit.
OR = Opal glass reflector.
F = Light filter.
M = Mirror.
E = Eye viewer.

According to the EPA methods manual, the only instrument meeting these criteria is the Hach Turbidimeter, Model 2100 and 2100 A (Ref. 5, p. 309-310). The Hach Model 2100, or equivalent, is used in the method for turbidity measurements given in the U.S. Geological Survey (USGS) manual on techniques of investigating water resources (Ref. 6, p. 157).

Additional information on turbidity methods by scattering can be found in the article "Measurement of Low Turbidities," by Black and Hannah (Ref. 8), and in Standard Methods (Ref. 3).

2. Transmittance

Methods based on measuring changes in the percentage of light transmitted are also used in turbidimeters. They can be applied to waters with high turbidity; waters with low turbidity require too long a path length for appreciable reduction in the intensity of the incident beam. These instruments are also called transmissometers, and can be used in the field to measure water transparency to depths down to at least 680 meters (2,000 feet). They measure water clarity, sediment suspension, plankton concentration and visibility for underwater television and photography.

2.1 Immersion

Angelo Secchi, an astrophysicist, was perhaps the first man to make measurements of the transparency of lake water. While on a papal yacht in 1865, he lowered a dinner plate into the water and noted the depth at which it was just visible. This "Secchi Disc" method is still used today; readings are given in depth units (centimeters and meters). The range of reading varies from a few centimeters in very turbid lakes to 40 meters in a clear lake such as Crater Lake, Oregon. A 20 cm diameter disc is most commonly used although diameters up to 1 meter have been reported. The disc is usually white, but may be divided into alternately painted black and white quadrants. Outdoor lighting affects readings so that observations should not be made in early morning or late afternoon and must be made through a shaded area of water surface. The Secchi disc disappears at a depth where the solar radiation has been reduced to about 5% of that at the surface. Precision of this method for measuring transmission is low, apparently because of such affects as variations in bottom conditions (color, smoothness, etc.), and side and surface scattering. The method has the advantage of simplicity and comparative inexpensiveness.

An immersion method used by the U.S. Geological Survey in the field for turbidity measurement consists of a graduated 8 in. long aluminum strip attached to a special 4 ft long non-stretchable water-resistant tape. Both tape and strip are graduated. See Figure B-8. A platinum needle and screw-eye are at the lower end of the aluminum strip. The scale is then immersed in the water until the platinum needle just disappears. The scale reading at the surface of the water then indicates the degree of turbidity. The scale is calibrated to read in units of ppm silica, and covers the range 7 to 3000 ppm.

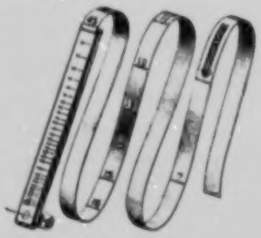


FIGURE B-8. Portable aluminum strip used to measure turbidity in the field (Ref. 10).

2.2 Light Absorption

Besides the visual methods, light transmission in water can be measured at various depths using instruments with photodetector tubes. One instrument is the Enviroline Model EV 4 Envirotrans underwater turbidimeter manufactured by Beckman Instruments. The submersible portion contains a light source, 10 cm long light path, and a photocell for converting light intensity readings to an electrical signal. The signal is recorded on the panel meter of a battery powered surface unit held by the operator out of the water. Readings may be made to a depth of 15 meters (50 feet).

The Hydro Products Model 612S Transmissometer System is submersible, and can be towed from a moving boat. A light projector unit and a detector unit are housed in a submersible sensor. A deck unit contains the meter used for logging turbidity measurements.

In studies of waters suitable for fish, a system of measurement sometimes used is based on the depth at which the light intensity is one millionth that at the surface. This depth is called the "millionth intensity depth" (m.i.d.). Light penetration may also be measured by irradiance meters, transmissometers, and hydrophotometers; all of which read in percent transmission. These light penetration measurements are not necessarily directly relatable to turbidity readings.

3. Continuous Monitors

Instruments are available for measuring turbidity in water continuously. These include those which measure changes in either percent transmission (or optical density) or intensity of scattered light. One example is the Hach Model 1292 Falling Stream Turbidimeter in which the water sample is designed to flow in a smooth flat stream through the light beam. See Figure B-9 (Ref. 11).

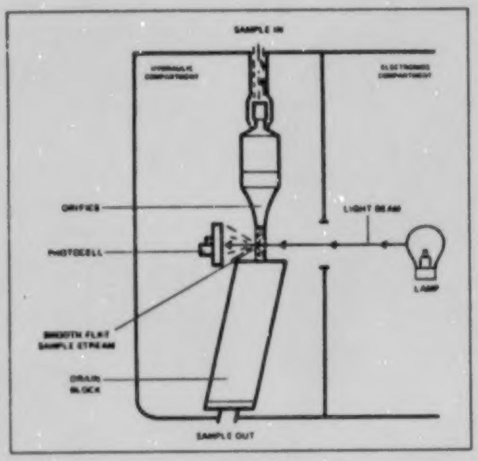


FIGURE B-9. Schematic of Hach Model 1292 Falling Stream Turbidimeter (Ref. 11).

As shown in Figure B-9, no parts of the optical system contact the flowing sample, cleaning is thus minimal. This instrument measures the light absorption of the sample and is not a nephelometer. Turbidity values are determined by laboratory calibration of each different type of water sample to be monitored. According to the manufacturer, the instrument can measure turbidities up to 10,000 units. It can be applied to measurements including the discharge of sewage sludge, coal content in washings, clay suspensions, and whey dumps from creameries and dairies (Ref. 11).

The Hach Model 2411, "Surface Scatter 3" Turbidimeter measures turbidity by surface scattering techniques. A light beam is directed at an acute angle to the surface of the water sample which overflows a pipe. See Figure B-10. Reflected and refracted light is dissipated by baffles and absorbers, while part of the scattered light is measured by a photo cell directly above the surface of the flowing water. Since only the light beam comes in contact with the water surface, windows are less likely to be fouled and cleaning of the optical surfaces is minimized. This surface scattering technique permits turbidity readings to be made over a wide range: From less than 0.2 to about 5000 units (Ref. 12).

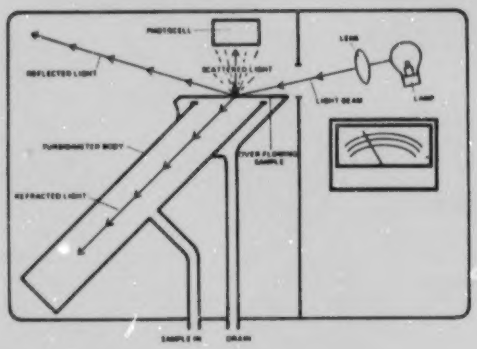


FIGURE B-10. Schematic of Hach Model 2411 Surface Scatter 3 Turbidimeter (Ref. 12).

4. Other

Recent techniques for measuring the mass concentration of suspended solids include a laboratory study on depolarization of backscattered polarized radiation (Ref. 13). This approach is based on the fact that the depolarization of scattered light resulting from multiple scattering increases with the concentration of scattering particles. An advantage of this method cited by the author is that correlation between the degree of depolarization and the weight concentration of suspended solids may be obtained if the density of the solids is determined. See Figure B-11.

Instrumentation components used included a mercury lamp as the source of polychromatic radiation; a Polaroid polarizer; and two light detectors. See Figure B-12 for a schematic of the instrumental arrangement. The backscattering angle used was 170°.

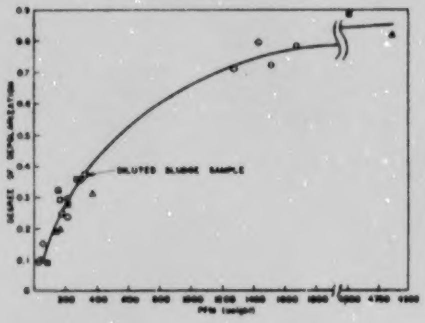


FIGURE B-11. *Degree of depolarization as a function of suspended solids. Wavelength of Incident radiation equals polychromatic light (Ref. 13).*

Scattering angle = 170°

- □ *Middlesex samples collected 5/23/69*
- ◇ *Middlesex samples collected 5/27/69*
- ○ *Bernardsville samples collected 6/10/69*
- ⬯ *Bernardsville samples collected 6/13/69*
- △ *Middlesex samples collected 6/17/69*
- ⊠ *Bernardsville samples collected 6/20/69*

The degree of depolarization was determined by measuring simultaneously 1/2 depolarized component with one detector, polarized plus 1/2 depolarized component with the other detector, and determining the ratio. Each detector contained a Polaroid analyzer and a 1P21 photomultiplier tube.

The technique was evaluated on suspensions prepared from polystyrene (Ref. 14) and on sewage samples. (Ref. 13). For the sewage samples, the concentration of suspended solids was determined by filtering successively through 10 µm and 0.3 µm membrane filters, followed by drying and weighing the filtered residues (Ref. 13).

Another laboratory instrument utilizing the effect of depolarization of polarized light due to scattering by a turbid medium used a laser light source (Ref. 15). Polarized light from the laser source is collimated and reflected at an angle to the turbid medium by a mirror. Light scattered back at about a 90° angle was detected and resolved into two components: $I_{//}$ with polarization having the same orientation with respect to the scattering plane as the incident polarization; and, $I_{\perp}$ the component of radiance with orthogonal polarization. Measurements were carried out for incident radiation both parallel and perpendicular to the scattering plane. See Figure B-13.

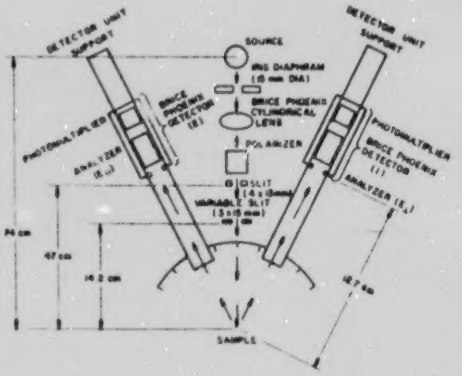

DETECTOR UNIT SUPPORT
SOURCE
IRIS DIAPHRAGM (6 mm DIA)
BRICE PHOENIX DETECTOR (Ɛ)
BRICE PHOENIX CYLINDRICAL LENS
PHOTOMULTIPLIER
POLARIZER
ANALYZER (E//)
SLIT (4 x 16 mm)
VARIABLE SLIT (3 x 16 mm)
DETECTOR UNIT SUPPORT
PHOTOMULTIPLIER
BRICE PHOENIX DETECTOR (I)
ANALYZER (E⊥)
96 cm
47 cm
16.2 cm
12.7 cm
SAMPLE

FIGURE B-12. *Schematic of instrumental arrangement for depolarization measurements at a back-scattering angle of 170° (Ref. 13).*

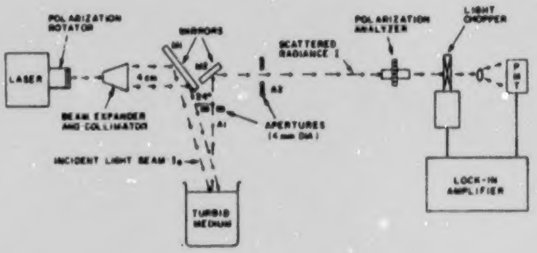

POLARIZATION ROTATOR
LASER
MIRRORS
M1
M2
4 cm
34°
BEAM EXPANDER AND COLLIMATOR
SCATTERED RADIANCE I
A2
A1
APERTURES (4 mm DIA)
POLARIZATION ANALYZER
LIGHT CHOPPER
PMT
INCIDENT LIGHT BEAM I₀
TURBID MEDIUM
LOCK-IN AMPLIFIER

FIGURE B-13. *Expermental arrangement. (Dimensions of turbid water were 6 cm high and 12 cm in diameter. Distance from water surface to aperture A1 was 10 cm. Distance along ray path from aperture A1 to aperture A2 was 25 cm.) (Ref. 15).*

The ratio $I_{//}/I_{\perp}$ was then plotted as a function of $[1 + 79(\rho_A/\rho_S)]^{-1}$, where ρ_S is the number of grams of suspended particles per ml, and ρ_A is the number of grams of coloring dye per ml added to the water. In this case, the suspended particles were Teflon (mean particle diameter 170 nm), and a black color dye (nigrosine black) that absorbs light was used.

For zero dye concentration, the ratio $I_{//}/I_{\perp}$ becomes unity: The condition of complete polarization. For larger dye concentrations, absorption increases in strength relative to scattering and the ratio $I_{//}/I_{\perp}$ rises sharply reflecting the decreasing contribution of multiple scatter events. The depolarization ratio $I_{//}/I_{\perp}$ is a very sensitive function of the ratio ρ_A/ρ_S. As black dye was added to the turbid water, the ratio ρ_S/ρ_A decreased, both $I_{//}$ and $I_{\perp}$ decreased but $I_{\perp}$ was found to decrease at a much faster rate than $I_{//}$.

This effect (more rapid decrease of $I_{\perp}$ as compared to $I_{//}$) can be of significance for monitoring a polluting effluent of light-scattering particles into dark river water. If the water were illuminated with polarized light, aerial photographs of $I_{\perp}$ would define the region of highest pollutant concentration (i.e., highest ρ_S/ρ_A) much more sharply than $I_{//}$. It may be possible to obtain a map of pollutant concentration in a stream from the data on the ratio $I_{//}/I_{\perp}$

From the standpoint of aerial surveillance of light scattering particles in water, a laser light source is better than natural skylight. This is because the polarization of skylight varies with position in the sky, so that various polarizations would focus onto a particular volume of water. A laser beam could be unambiguously polarized. It could be differentiated from natural polarized skylight by modulating (chopping) the incident laser beam, and detecting $I_{//}$ and $I_{\perp}$ using lock-in amplification. (Ref. 15).

C. SUMMARY AND RECOMMENDATIONS

Visual methods for measuring turbidity and/or light transmission such as the Secchi disc, USGS platinum pin, Jackson candle, and use of bottle standards have limited range and low sensitivity, precision and accuracy. They do have the virtue of low cost, portability, little or no electric power requirements, and a long history of use. With proper calibration techniques and interpretation they are useful and sufficient for applications including those where only in-house comparisons of samples are desired.

The nephelometric methods of measuring turbidity are sensitive to the light scattering properties of the particles causing the turbidity. Particle size, shape, and refractive index affect light scattering and thus measurements. The Formazin polymer suspension is recommended as the standardizing turbidity suspension for calibration of many instruments because it can be uniformly reproduced. The 90° nephelometric technique is the basis for many commercial turbidity instruments but there is no direct relationship between Jackson Candle Turbidity and the 90° nephelometer (Ref. 3) for fundamental reasons. The Jackson Candle Turbidimeter uses a forward-scattering method: It can be more sensitive to large particles than a side-scattering instrument (Ref. 7, 8). Furthermore, the candle turbidimeter will not measure fine particles or black particles, whereas instruments with a light bulb source are more likely to detect these particles.

Forward-scatter on-line instruments have advantages including higher intensity of scattered light, greater sensitivity to large particles and less error due to dissolved color (if the ratio method is used) than side-scattering instruments. However, the cost is greater and the measurement angle is more critical for forward-scattering than with side-scattering instrumentation.

Interferences in turbidimeters include the following:

1) dirty surfaces in the measuring path,
2) bubbles of all sizes in the water,
3) dissolved color in the water, and
4) scratched or cracked glass optics.

Preparation of turbidiy standards is important because results are calculated from calibration plots. Reproducible purity of hexamethylenetetramine and hydrazine sulfate is essential and materials of highest purity should be used.

In any of the above methods, there is no correlation between the measured intensity of scattered light and the concentration of dissolved solids. There may be a correlation, if depolarized light techniques are used.

Manufacturers of turbidimeters should evaluate light depolarization techniques for any advantages: (1) the intensity of scattered light may correlate with the concentration of dissolved solids in sewage, (2) continuous analyzers may be developed using modulated laser light source which is sufficiently removed from the stream being monitored so that optics are not dirtied.

D. REFERENCES

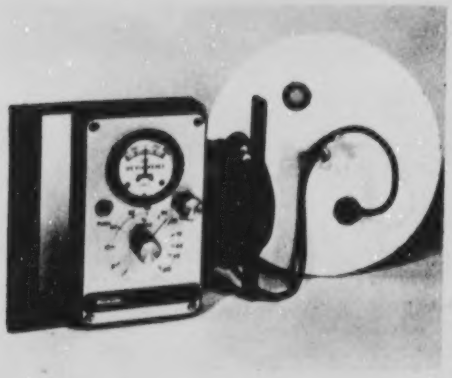
1. *Water Quality and Treatment, A Handbook of Public Water Supplies*, 3rd Edition, The American Water Works Association, Inc., McGraw-Hill Book Co., New York, NY (1971).
2. *Water Quality Criteria*, Federal Water Pollution Control Administration, Department of Interior, Washington, DC 20242 (1968).
3. *Standard Methods for the Examination of Water and Wastewater*, 13th Edition, American Public Health Association, Washington, DC 20036 (1971).
4. *Domestic Water Supplies Quality and Monitoring*, Laws and Regulations, State of California, Department of Public Health, 2151 Berkeley Way, Berkeley, CA 94704, Title 17 (Register 72, No. 32-8-5-72).
5. *Methods for the Chemical Analysis of Water and Wastes*, Environmental Protection Agency, Cincinnati, OH 45268 (1971).
6. *Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases*, USGS, Department of Interior, Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402 (1970).
7. R.J. Simms, "Industrial Turbidity Measurement," *ISA Transactions*, *11* (2), 146 (1972).
8. A.P. Black and S.A. Hannah, "Measurement of Low Turbidities," J. Am. Water Works Assoc., *57*, 901 (1965).
9. C.C. Hach, "Turbidity and Nephelometry," Medical Electronics and Data, September-October, 1970.
10. *Catalog No. 62*, Hellige, Inc., Garden City, NY 11530 (1970).
11. Manufacturer's Bulletin, 1031/1292 2ED "Falling Stream Turbidimeters," Hach Chemical Company, P.O. Box 907, Ames, IA 50010.
12. Manufacturer's Bulletin, 2411-1ED, "Surface Scatter 3 Turbidimeter ," Hach Chemical Company, P.O. Box 907, Ames, IA 50010.
13. J.W. Liskowitz and G.F. Franey, "Measurement of Suspended Solids Concentrations in Sewage by Use of a Depolarization Method," Env. Sci. Tech., *6* (1), 43 (1972).
14. J.W. Liskowitz, "An Empirical Method for Determining the Concentration of Solids in Suspension," Env. Sci. Tech., *5* (12), 1206 (1971).
15. "Depolarization of Laser Light Scattered from Turbid Water," V.L. Granatstein, M. Rhinewine, and A.M. Levine, Applied Optics, *11* (8), 1870 (1972).

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

H2O-PHY
Field: TUR
Beckman 1
February 1973

Light Transmission

Enviroline Model EV3 Electronic Secchi Disc



Class	Continuous-Sensor
Categories of Water	Fresh, Saline, and Waste
Principle of Operation	(1) The Secchi disk is lowered into the water, and the depth at which it is no longer visually observed is recorded. (2) The amount of natural light transmitted from the surface to a photocell may also be measured as a function of depth. Depth limit is 15 meters (50 feet).
Minimum Detectable Sensitivity	Irradiance meter - ±2% transmission
Range	Irradiance meter - 1 to 100% transmission
Interferences	Bubbles or dirty optical surfaces can affect irradiance meter readings.
Multiparameter Capability	Secchi disk and % transmitted light from the surface
Sampling	Method: Sensor Volume: In-situ Maximum Temperature Input: Collection Efficiency: Maximum Number of Sample Sources: One
Performance	Accuracy: Irradiance meter - ±5% transmission Reproducibility: Irradiance meter - ±2% transmission Linearity: Noise: Lag Time: Rise Time: Retention Time: Fall Time: Zero Drift: Span Drift:

Operation

Ambient Temperature Range: 0 to 38°C
Temperature Compensation:
Relative Humidity Range: 0-90%
Calibration: Manual, before each measurement
Procedure:
Unattended Period:
Maintenance: Change batteries as required. Clean optical surfaces.

Requirements

Power: Irradiance meter - 4 penlight batteries (Size AA)
Weight: Irradiance meter - 1.82 kg (4 lb)
Secchi disk - 0.45 kg (1 lb)
Dimensions: Irradiance meter - 15.2 cm x 10 cm x 20 cm (6" x 4" x 8")
Secchi disk - 21.6 cm dia. (8.5")

Features

Output: Manually adjusted dial
Training: Minimal required; manual included
Options:

References

(a) Manufacturer's Brochure "Enviroline Model EV3 Enviroeye Electronic Secchi Disk"
(b) Manufacturer's price list, February 15, 1973
(c) Letter from manufacturer, January 4, 1973

Cost

$137 F.O.B. Destination

Remarks

Permanently installed Kodak No. 57 green filter.

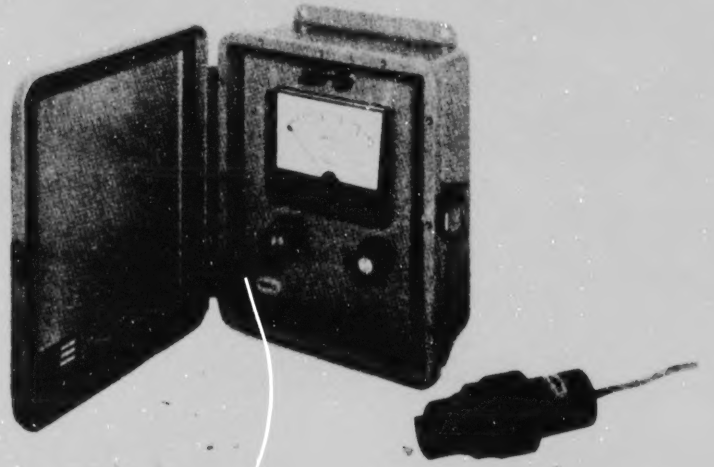
Address

Beckman Instruments, Incorporated
Cedar Grove Operations
89 Commerce Road
Cedar Grove, NJ 07009
Attn: Charles A. Soumas
(201) 239-6200

H2O-PHY
Field: TUR
Ecologic 1
February 1973

Nephelometer

Ecologic Model 204 Analyzer
(Turbidity)



Class	Continuous-Sensor
Categories of Water	Fresh, Waste, and Saline
Principle of Operation	Polychromatic light from a single source is passed through the sample, and intensity of light scattered at approximately right angles to the incident light is measured by a silicon semiconductor detector. The instrument uses a dual beam approach to minimize the effects of the light source.
Minimum Detectable Sensitivity	15 JCU
Range	Model 204-1, 0-15 and 0-150 Model 204-2, 0-150 and 0-1500 Model 204-3, 0-1500 and 0-3000
Interferences	None: Dual beam, dual detector ratio method automatically compensates out bubbles, color, scratches.
Multiparameter Capability	
Sampling	Method: Continuous Volume: Minimum of 200 ml Maximum Temperature Input: 49°C Collection Efficiency: Maximum Number of Sample Sources: One
Performance	Accuracy: ±5% full scale is standard, ±2% is optional Reproducibility: ±1% Linearity: ±3% Noise: 1 JTU Lag Time: Rise Time: <30 sec response time Retention Time: Fall Time: Zero Drift: <2% per week Span Drift: <1% per week

Operation

Ambient Temperature Range: 0-66°C
Temperature Compensation: Automatic T.C.
Relative Humidity Range: To 100%
Calibration: Static method for side-scattering nephelometers given in Standard Methods uses formazin. (See Reference c.)
Procedure: Set sensor into standard formazin suspensions and record readings (static method).
Unattended Period: 30 days
Maintenance:

Requirements

Power: 115 or 220 Vac; 50/60 Hz
Weight: 5.5 kg net (12 lb)
Dimensions: 29.2 cm H x 23.5 cm W x 11.5 cm D (11-1/2" x 9-1/4" x 4-1/2")

Features

Output:
Training:
Options:

(1)	Auto-probe cleaning (Model 204SC)	$240
(2)	High or low alarm contact (Model 204SC)	$150
(3)	Remote meter indicator, up to 1525 meters (5000 feet)	$350

References

(a) Manufacturer's Bulletin 204, August 1971.
(b) Manufacturer's letter, dated November 27, 1972; March 13, 1973.
(c) Standard Methods for the Examination of Water and Wastewater, 13th Edition, American Public Health Association, Washington, DC 20036 (1971).

Cost

$875

Remarks

Above information obtained from manufacturer. Submersible sensor to 30.5 m (100 ft) depths.

Address

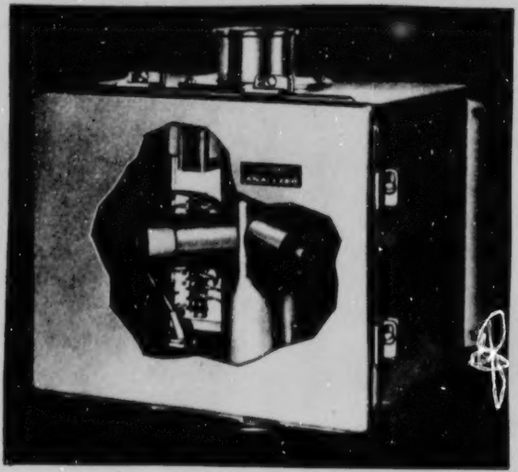
Ecologic Instrument Corporation
597 Old Willets Path
Hauppauge, NY 11787
(516) 582-4110
Attn: R.A. Gabriele, President
M. Rothman, V.P. Engineering

H2O-PHY
Field: TUR
GAM RAD 1
February 1973

Side-Scatter Nephelometer

GAM RAD Inc. Model 260 Fluid Analyzer

MICROAMPERES
FLUID ANALYZER
GAM RAD, INC.



Class	Continuous-Sensor
Categories of Water	Fresh, Waste, and Saline
Principle of Operation	Polychromatic light from a tungsten lamp source is passed through the flowing sample stream. The intensity of the light scattered at about 90° angle from the incident light is monitored by a CdS photocell, which converts the light into an electric signal. The intensity of the signal is taken as a measure of the turbidity of the sample stream, and is logged onto a meter for visual readout. Remote operation is possible because the meter (control station) can be located as far as 152 meters (500 feet) from the sensor. This unit maybe converted to the absorption mode for selected turbidity ranges.
Minimum Detectable Sensitivity	50 ppb
Range	50 ppb to 50,000 ppm
Interferences	Dissolved color can cause low readings. Air or gas bubbles, scratched optics can cause high readings.
Multiparameter Capability	None
Sampling	Method: Continuous Volume: 283.9 liters per minute (75 gallons per minute) flow rate Maximum Temperature Input: 60°C (140°F) Collection Efficiency: Maximum Number of Sample Sources: Multiple
Performance	Accuracy: ±2% full scale Reproducibility: ±1% Linearity: Depends on range of measurement Noise: Nil Lag Time:) Rise Time:) Retention Time:) A function of flow rate Fall Time:)

Performance (Cont'd)

Zero Drift:
Span Drift:

Operation

Ambient Temperature Range: -18° to + 60°C (0 to 140°F)
Temperature Compensation:
Relative Humidity Range:
Calibration: Before installation; using Formazin
Procedure: A fixed reference standard
Unattended Period: 1 to 6 months, varies with application
Maintenance: 2 to 4 times per year

Requirements

Power: 117 Vac, 50-60 Hz, 150 W maximum
Weight: Sensor - about 16 kg (35 lb)
Control - about 9 kg (20 lb)
Dimensions: Sensor - 35.6 cm W x 25.4 cm H x 25.4 cm D (14" x 10" x 10")
Control - 30.5 cm W x 23.5 cm H x 24.2 cm D (12" x 9-1/4" x 9-1/2")

Features

Output: Meter (See "Options")
Training:
Options: Data may be recorded onto:
(a) Recorder or Controller)
(b) Alarm)
(c) Computer or Logger)
(d) Auxiliary Amplifier)

Accessories can include:
(a) Panel-Mounted Indicator)
(b) Dust and Vapor tight miniature panel-mounted indicator) These items quoted on request
(c) Sight-Port Assembly)
(d) Extra Connecting Cable)
(e) 5.08 cm (2") NPT Adapter)
(f) Synthetic Sapphire Windows)
(g) Explosion-Proof Sensing Station)
(h) Special Coatings on all wetted surfaces (PVC, Teflon, etc.))
(i) Special Materials of Construction (Titanium, 316 Stainless Steel))
(j) Others, for special requirements)

References

(a) Manufacturer's brochure, Bulletin T-100.
(b) Manufacturer's brochure, Bulletin T-400.
(c) Letter from manufacturer, November 14, 1972 and March 7, 1973.

Cost

$1600 for basic system

Remarks

Manufacturer has a color compensation accessory available as an optional feature. Attention should be given by the user to maintaining proper calibration of the sensor and control units after installation. For a static calibration procedure, see Standard Methods for the Examination of Water and Wastewater, 13th Edition, American Public Health Association, Washington, DC 20036 (1971).

Address

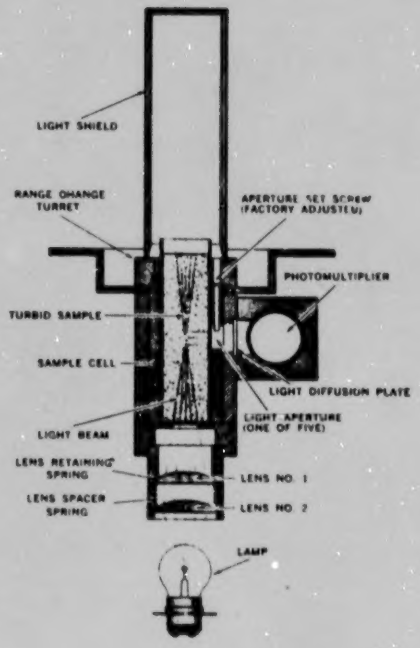
GAM RAD, Incorporated
16825 Wyoming Avenue
Detroit, MI 48221
Attn: W.E. Helke
(313) 864-6006

H2O-PHY
Laboratory: TUR
Hach 1
February 1973

Light-Scattering Nephelometer

Hach Laboratory Turbidimeter - Model 2100A

HACH
MODEL 2100A
TURBIDIMETER


LIGHT SHIELD
RANGE CHANGE TURRET
APERTURE SET SCREW (FACTORY ADJUSTED)
PHOTOMULTIPLIER
TURBID SAMPLE
SAMPLE CELL
LIGHT DIFFUSION PLATE
LIGHT BEAM
LIGHT APERTURE (ONE OF FIVE)
LENS RETAINING SPRING
LENS NO. 1
LENS SPACER SPRING
LENS NO. 2
LAMP

Light-path of Model 2100.

Class:	Laboratory Analysis
Categories of Water	Fresh, Waste, Saline
Principle of Operation	Incident light from a polychromatic source (tungsten lamp, UV-VIS range) is passed upward through a flat-bottomed tube containing the water sample. A portion of this incident light is scattered by suspended material in the sample and is detected at approximately a right angle to the incident light by a photomultiplier tube. The signal is amplified and logged onto a direct reading meter scale. The intensity of the scattered light is taken as a measure of the turbidity of the water sample. Meter readings are converted to turbidity units by calibration data. Samples must be well-mixed, and should not have any bubbles.
Minimum Detectable Sensitivity	0.04 units.
Range	0-0.2; 0-1.0; 0-10; 0-100; 0-1000 Samples with readings >1000 can be diluted so that they will fall on scale.
Interferences:	Samples with dissolved color which absorb light can give low readings; bubbles can cause high readings; scratches on sample tubes can scatter light and cause high readings; dirty sample tubes can also scatter light and cause high readings. Units available to remove color interferences.
Multiparameter Capability	Chloride, turbidity

Sampling

Method: Batch sample should be analyzed as soon as possible after being obtained.
Volume: 25 ± 1 ml

Maximum Temperature Input: Not applicable
Collection Efficiency: Not applicable

Performance

Accuracy: ±2% of full scale except ±10% for 0-1 scale
Reproducibility: ±2% of full scale
Linearity: Over ranges indicated ,±1%
Noise:
Lag Time:
Rise Time: <1 sec (Response Time)
Retention Time:
Fall Time:
Zero Drift: 0.01 FTU max (10° - 40°C)
Span Drift: 0.5% max (10° - 40°C)

Operation:

Ambient Temperature Range: 0° - 50°C
Temperature Compensation: None
Relative Humidity Range: 99% RH
Calibration: Standard suspension prepared by mixing solutions of hexamethylenetetramine and hydrazine sulfate are used. (See H2O-PHY, Turbidity) These are called formazin suspensions. Liquid latex secondary standards available.
Procedure: Standard suspensions covering the turbidity range of interest are measured by the nephelometer. Meter readings are plotted versus suspension concentrations (in turbidity units).
Unattended Period: Leave instrument on (unless not used for one month)
Maintenance: Minimal

Requirements

Power: 95-135 VAC; 50-60 Hz; 35 W or 190-270 VAC; 50-60 Hz; 35 W
Weight: (Net) 7.7 kg (17 lb)
Dimensions: 30.5 cm W x 22.9 cm H x 21.6 cm D (12" W x 9" H x 8-1/2" D)

Features

Output:
Training: very little required
Options:

References

1. Manufacturer's brochure, Bulletin 2100A-2ED, 5-15-71-M
2. "Turbidity and Nephelometry", C.C. Hach, Medical Electronics and Data, Sept., Oct. 1970
3. "Clean Water, Methods for Chemical Analysis of Water and Wastes," Environmental Protection Agency Bulletin 16020...07/71.
4. Manufacturer's letter, Feb. 28, 1973.

Cost

$525

Remarks

Accessories included with Model 2100A:
- 4 sample cells, 25 mm
- 1 cell riser
- Set of 4 liquid latex standards
- 1 focusing template
- 1 dust cover
- 1 light shield
- 1 instruction manual

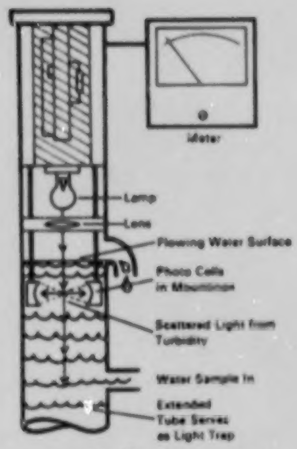
One year warranty against defects except 90 days for photomultiplier tube.

Address

Hach Chemical Company
P.O. Box 907
Ames, IA 50010
(515) 232-2533

Nephelometer for Turbidity Measurements

Hach Model 1720 Low Range Turbidimeter


Meter
Lamp
Lens
Flowing Water Surface
Photo Cells
in Mountings
Scattered Light from
Turbidity
Water Sample In
Extended
Tube Serves
as Light Trap

Low Range
Turbidimeter, Model 1720

MASTER INDICATOR
(locate near turbidimeter)

Class	Continuous - sensor
Categories of Water	Fresh, Saline, Waste
Principle of Operation	The water stream being monitored flows continuously through the nephelometer, past an intense light source. Light scattered at right angles by suspended particles is detected by two hermetically sealed photoconductive cells. The intensity of the scattered light is logged on a meter scale or on a pen-and-ink strip chart recorder. The meter or recorder readings are related to turbidity by means of calibration data.
Minimum Detectable Sensitivity	0.05 FTU
Range	0-0.2, 1.0, 3.0, 30.0 FTU
Interferences	Bubbles in the liquid and stray light deflected to the detector by scratches, glass imperfections or dirt can cause high readings. Dissolved color which absorbs light from the source causes low results due to reduction in intensity of the light source.
Multiparameter Capability	None
Sampling	Method: Continuous Volume: 0.95 to 1.89 liter per minute (1/4 to 1/2 gallon per minute) Maximum Temperature Input: 45°C Collection Efficiency: Maximum Number of Sample Sources: One

Performance

Accuracy: ±5%
Reproducibility: ±2%
Linearity: Non-linear
Noise:
Response Time: 30 seconds to detect a change in turbidity
Retention Time:
Fall Time:
Zero Drift:
Span Drift:

Operation

Ambient Temperature Range: to 45°C
Temperature Compensation: None
Relative Humidity Range: 99%
Calibration: After installation, a standard reflectance rod (equivalent to 5.0 JTU) is inserted through an entrance port on the side of the turbidimeter. The instrument is adjusted to read a difference of 5.0 JTU when the reflectance rod is in and out of the light beam.
Procedure: The water stream being monitored is passed through the Model 1720. Meter or recorder readings of any turbidity changes are logged.
Unattended Period:
Maintenance: Photocells should rarely require cleaning (depending on sample water screen). Only periodic checks of the instrument calibration should be required.

Requirements

Power: 100-135 Vac; 60 Hz; 20 Watts
Weight: 10.9 kg (24 lbs): less master indicator
Dimensions: Turbidimeter body: 81.5 cm long, 10.5 cm diameter (32", 4-1/8").
Master Indicator Case: 17.2 cm H x 13.3 cm W x 3.2 cm D (6-3/4" x 5-1/4" x 1-1/4").

Features

Output: Meter, Strip Chart Recorder, or Alarm.
Training:
Options:

1722-00	Remote Indicator	$ 95
1064-00	Floor Stand	$ 40
6491-00	Recorder, 100 μ-A, 5.08 cm (2") chart, 115 Vac, 60 Hz	$127
6495-00	Recorder Alarm, 100 μ-A, 5.08 cm (2") chart, 115 Vac, 60 Hz	$222
3563-03	Bubble Trap, PVC construction	$ 50
5740-00	Recorder shunt, for recorders with inputs less than 470 mv dc (specify value)	$ 30

References

(1) Manufacturer's brochure Bulletin 1720-3ED, "Continuous Reading Low Range Turbidimeter Model 1720", 12/1/71.
(2) Manufacturer's letter, dated Nov. 9, 1972 (received); comments, April 1973.

Cost

$495 for Model 1720 without options.

Remarks

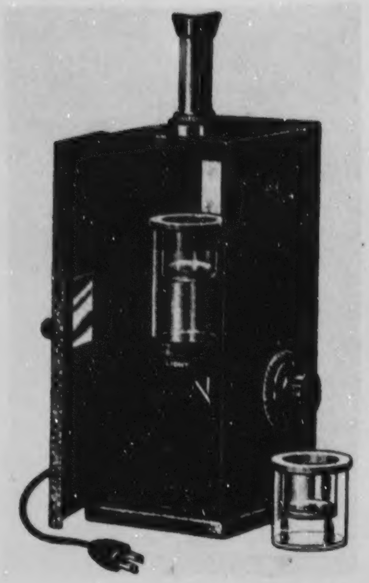
Above information taken from References (1) and (2). The Model 1720 has been applied to monitoring turbidity of "red water" in distribution systems. See M. Buck, "Turbidimetric Monitoring of Red Water in Distribution Systems", Water and Sewage Works, December 1969.

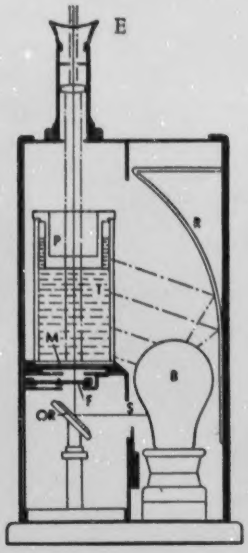
Address

Hach Chemical Company
P.O. Box 907
Ames, IA 50012
(515) 232-2533
Attn: Arlene Justing, Marketing Communications

Side-Scatter Nephelometer

Hellige Model 8000-T Turbidimeter





B. Bulb
R. Reflector
T. Turbidimeter tube
P. Plunger
S. Slit
F. Filter
OR. Reflector
M. Mirror
E. Eyepiece

Class	Laboratory Analysis
Categories of Water	Fresh, Waste, and Saline
Principle of Operation	A light beam from an opal glass bulb is directed by a mirror upward through a tube containing the water sample to an ocular eyepiece. This light is not appreciably reduced in intensity, and is viewed head-on by the ocular where it appears as an inner circle in the eyepiece. Another mirror reflects light from the bulb to the side of the sample tube where it is scattered by the particles causing turbidity. The scattered light is observed from the side of the incident light by the same ocular eyepiece; it appears as the outer portion of the circular split-field. The center of the field as seen in the eyepiece will be lighter or darker than the outer field, depending on the amount of light permitted to pass through the head-on direction by an adjustable slit. Movement of a vernier dial changes the slit width and thus the light intensity until the inner and outer portions of the split field seen in the ocular eyepiece appear identical. The reading of the vernier is taken as a measure of turbidity, and is related to turbidity units by calibration data.
Minimum Detectable Sensitivity	0.05 units
Range	0 to 150 units
Interferences	Dissolved color can affect reading. Bubbles, dirty or scratched optical surfaces can cause high readings.
Multiparameter Capability	Sulfate (Model 8000TS)

Sampling

Method: Batch sampling
Volume: 130 ml sample
Maximum Temperature Input:
Collection Efficiency: 100%
Maximum Number of Sample Sources: One

Performance

Accuracy: ±2%
Reproducibility: ±2%
Linearity:
Noise:
Response Time:
Retention Time:
Fall Time:
Zero Drift:
Span Drift:

Operation

Ambient Temperature Range:
Temperature Compensation: None
Relative Humidity Range:
Calibration: Calibrated using suspensions of known turbidity. Can be factory calibrated using silica or uncalibrated (Model 8000 U). Standard Methods (see references) uses Formazin standards for calibration of side-scattering nephelometers.
Procedure: Water sample is placed in the turbidimeter tube, and the tube set inside the turbidimeter. The dial is rotated until the two fields viewed in the eyepiece appear of equal intensity. The dial reading is recorded by the operator, and converted to turbidity units using calibration data. (See Instruction Manual from manufacturer.)
Unattended Period: Laboratory instrument.
Maintenance: Optical glass bottom of turbidimeter tube must be cleaned if dirty; replaced, if scratched.

Requirements

Power: 110-130 Vdc or Vac; 60 Watts; 50-60 Hz
Weight: 3.6 kg (8 lb)
Dimensions: 15.2 cm W x 17.8 cm D x 40.6 cm H (6" W x 7" D x 16" H)

Features

Output: Dial reading
Training: Not necessary

Options: Model 8000-T, manufacturer calibrated for turbidity	$474.50
Model 8000-TS, manufacturer calibrated for turbidity and sulfate	$
Model 8000-U, uncalibrated	$

References

(1) Manufacturer's Catalog No. 62, June 1970.
(2) Manufacturer's letter, Nov. 27, 1972; letter, Feb. 27, 1973.
(3) Standard Methods for the Examination of Water and Wastewater, 13th Edition, American Public Health Association, Washington, DC 20036 (1971).

Cost

$474.50

Remarks

Model 8000-T price includes the following:
(a) Two pre-calibrated opal bulbs
(b) Calibration charts covering ranges, 0-1, 0-4, 0-15, 0-50, 0-150 units
(c) Optically polished viewing surface plunger
(d) Turbidimeter tubes and directions

Manufacturer supplies include:
(a) 14 Turbidity standard suspensions of 0, 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 80, 90, 100 ppm silica

#8050-S16, 16 oz bottles	$39
#8050-S32, 32 oz bottles	$57

Remarks (Continued)

(b) Individual suspension standard, any bottle,

R-749,	16 oz	$5
	32 oz	$7

(c) Stock suspension, 1000 ppm silica

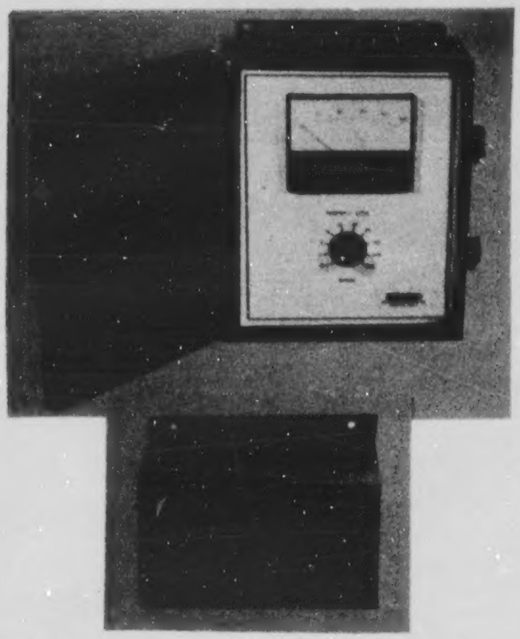
8 oz	$2.75
16 oz	$5.00
32 oz	$7.00

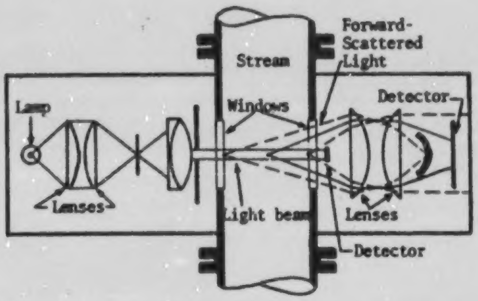
Address

Hellige, Incorporated
877 Stewart Avenue
Garden City, NY 11530
Attn: Barry Caplan
(516) 741-3300

Forward-Scattering Measurement Turbidimeter

Monitek Model 160/131 Slip-Stream Turbidimeter





Optical schematic for an in-line forward-scatter turbidimeter.

Class	Continuous-Sensor
Categories of Water	Waste, Fresh, Saline
Principle of Operation	A collimated 2-3 mm wide beam of white light from a tungsten source is passed through a slip-stream of the water being analyzed. The intensity of the beam that passes directly through the water is measured by a detector. This direct beam may be reduced in intensity by any dissolved color in the water, but is not significantly reduced in intensity by scattering effects to about 500 JTU. Light scattered by any turbidity in the forward direction at an angle of about 15° from the horizontal is measured by a scattered beam detector. The ratio of the intensities of the two beams is then computed by a converter unit, and read out on the meter.
Minimum Detectable Sensitivity	0.01 JTU
Range	0.5 to 500 JTU
Interferences	Dissolved color interference minimized by use of ratio readout. Bubbles interference minimized electronically by a reject circuit which discriminates against short, sharp pulses caused by bubbles.
Multiparameter Capability	None
Sampling	Method: Continuous (1/4" N.P.T. pipe connections) Volume: Depends on line size. Maximum line pressure is 90 lb. Maximum Temperature Input: 100°C Collection Efficiency: Maximum Number of Sample Sources: One

Performance

Accuracy: ±1%
Reproducibility: ±1% repeatability
Linearity: ±1%
Noise:
Lag Time:
Rise Time (Response Time): 0.001 sec
Retention Time:
Fall Time: 0.001 sec
Zero Drift: ±0.05 JTU within 10 min of switch on, ±0.005 JTU thereafter
Span Drift: ±1%

Operation

Ambient Temperature Range: 0 to 100°C
Temperature Compensation: None (not needed)
Relative Humidity Range: 0-100%
Calibration: Use diatomaceous earth to prepare standard suspension for calibration by manufacturer before shipment.
Procedure:
Unattended Period: Indefinite for clean liquid streams
Maintenance:

Requirements

Power: 110 V, 60 Hz, 25 W
Weight: 11.3 kg (25 lb) (Shipping weight)
Dimensions: 160 Transmitter -- 25.4 cm W x 15.2 cm H x 12.7 cm D (10" W x 6" H x 5" D)
131 Converter -- 35.6 cm H x 26.6 cm W x 12.7 cm D (14" H x 11" W x 5" D)

Features

Output: 0-10 V
Training: None required
Options: 4-20 mA output, air purge

References

(a) Manufacturer's Bulletin, "Monitek Model 160/131 Slip-Stream Turbidimeter."
(b) I.S.A. reprint 71-728, "Industrial Turbidity Measurements" by R. John Simms.
(c) Manufacturer's letter of Dec. 28, 1972.

Cost

$1575

Remarks

Forward-scatter instruments can have a higher output signal and can be more sensitive to large particles than side-scatter instruments. The ratio method can also minimize the effects of dissolved color on turbidity measurements. For a discussion of turbidity measurements, see A.P. Black and S.A. Hannah, "Measurement of Low Turbidities," J. Am. Water Works Assoc., 57 (7), 901 (1965).

Attention should be given by the user to maintaining proper calibration of the instrument after installation. For a static calibration procedure, see Standard Methods for the Examination of Water and Wastewater, 13th ed., American Public Health Association, Washington, DC 20036 (1971).

Address

Monitor Technology, Inc.
303 Convention Way
Redwood City, CA 94063
(415) 365-6550

Turbidity in Water

Monitek Model 150 Laboratory Turbidimeter

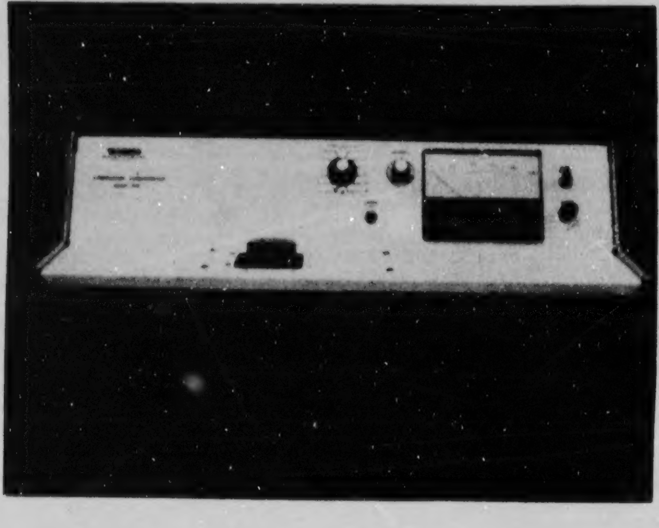
Class	Laboratory analysis
Categories of Water	Fresh, Saline, Waste
Principle of Operation	The water sample is placed into 50 ml test tube, and inserted into the sample well. A collimated beam of polychromatic white light is passed through the water sample: The intensity of light in the forward direction (direct light) is measured by a direct beam detector. Light scattered about 15° from the forward direction is measured by the scattered beam detector. The ratio of these two signals is electronically calculated and displayed on a panel meter. The meter reading is related to turbidity by means of calibration measurement.
Minimum Detectable Sensitivity	0.01 JTU
Range	0-0.5, 1, 2, 5, 10, 20, 50, 100, 200, 500
Interferences	Bubbles can interfere. Interferences due to dissolved color or stray light is eliminated.
Multiparameter Capability	Could be used for turbidimetric analyses (Cl^-, $SO_4^=$)
Sampling	Method: Batch Volume: 50 ml Maximum Temperature Input: 100°C Collection Efficiency: Maximum Number of Sample Sources: One

Performance	Accuracy: Reproducibility: Linearity: 1% full scale Noise: Lag Time: Rise Time: 0.001 sec Retention Time: Fall Time: 0.001 sec Zero Drift: ±0.05 JTU within 10 min of switch on, ±0.005 JTU thereafter Span Drift: None observed
Operation	Ambient Temperature Range: 0 to 100°C Temperature Compensation: None required Relative Humidity Range: 0 to 100% Calibration: Silica or Formazin standards. See Standard Methods for the Examination of Water and Wastewater, 13th edition, American Public Health Association, Washington, DC (1971), p. 351, 354 for static methods. Procedure: See Standard Methods, 13th edition Unattended Period: Maintenance:
Requirements	Power: 110 Vac, 60 Hz, 25 watts Weight: 4.5 kg (10 lb) shipping weight Dimensions: 27.9 cm x 17.8 cm x 17.8 cm (11" x 7" x 7")
Features	Output: Analog, panel meter; direct reading scale Training: Options:
References	(1) Manufacturer's brochure, "Monitek Model 150 Laboratory Turbidimeter," undated. (2) Manufacturer's letter, dated December 28, 1972. (3) Manufacturer's communication, April 6, 1973.
Cost	$675
Remarks	Warm-up time is 15 minutes. Information obtained from manufacturer; References 1, 2, 3.
Address	Monitor Technology, Inc. 303 Convention Way Redwood City, CA 94063 (415) 365-6550

H2O-PHY
Laboratory: TUR
Monitor Technology 3
April 1973

Turbidity in Water

Monitek Model 250 Laboratory Turbidimeter

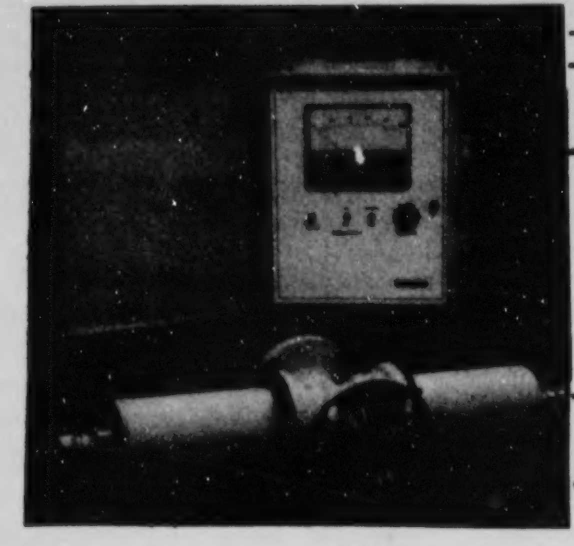


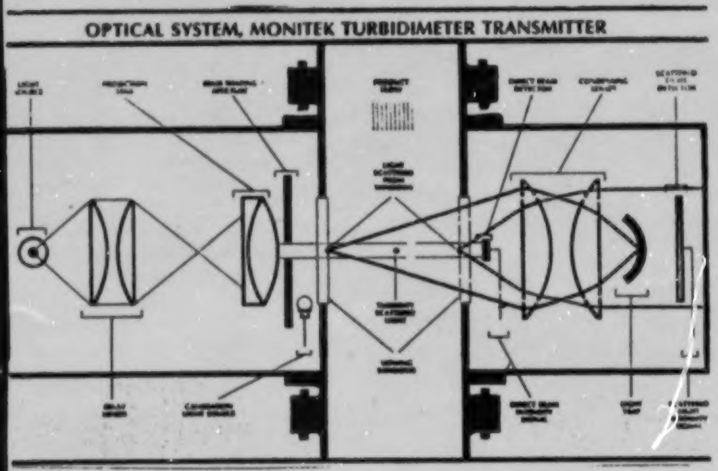
Class	Laboratory Analysis
Categories of Water	Fresh, Saline, Waste
Principle of Operation	A sample of the water to be tested is added to a bottle, and the bottle then inserted in the sample well of the instrument. A collimated beam of white light is passed through the sample of water: Light directly in the forward direction is measured by one detector (direct light), while light scattered at about 15° from the forward direction is measured by another detector. The ratio of the output from the two detectors is calculated electronically, and recorded on a meter. The meter reading is related to the turbidity of the sample from calibration data.
Minimum Detectable Sensitivity	0.005 ppm (silica standard scale)
Range	0.1 to 1000 ppm full scale
Interferences	The ratio method used corrects for loss in light intensity due to dissolved color in the water sample and changes in source intensity. Bubble-discriminating circuit rejects short, sharp pulses caused by bubbles to eliminate this source of interference.
Multiparameter Capability	Could be used for turbidimeter analyses (Cl^-, $SO_4^=$)
Sampling	Method: Batch, using 500 ml screw cap bottles Volume: 500 ml Maximum Temperature Input: Collection Efficiency: Maximum Number of Sample Sources: One

Performance	Accuracy: Reproducibility: Linearity: 1% full scale Noise: Lag Time: Rise Time: 100 milliseconds Retention Time: Fall Time: 100 milliseconds Zero Drift: <1% per day Span Drift: <1% per day
Operation	Ambient Temperature Range: 4.4°C to 48.9°C (40°F to 120°F) Temperature Compensation: None required Relative Humidity Range: 0 to 99% Calibration: Silica (or Formazin) Standards. See *Standard Methods for the Examination of Water and Wastewater*, 13th edition, American Public Health Association, Washington, DC (1971), p. 351, 354 for static calibration procedures. Procedure: See H2O-PHY, Turbidity Section Unattended Period: Maintenance:
Requirements	Power: 110/220 Vac; 50-60 Hz; 25 Watts Weight: 9 kg (20 lb) Dimensions: 30.5 cm H x 61 cm W x 22.9 cm D (12" x 24" x 9")
Features	Output: Analog panel meter Training: Not needed Options: Dry air purge of sample chamber
References	(1) Manufacturer's brochure: Monitek Model 250 Laboratory Turbidimeter (undated). (2) Manufacturer's letter, dated December 28, 1972. (3) A.P. Black and S.H. Hannah, "Measurement of Low Turbidities," J. Am. Water Works Assn., 57(7), 901 (1965). (4) Manufacturer's communication, April 6, 1973.
Cost	$1850
Remarks	
Address	Monitor Technology, Inc. 303 Convention Way Redwood City, CA 94063 (415) 365-6550

Turbidimeter

Monitek Industrial Turbidimeters, Model 215, 210 Transmitters
Model 130 Converter





Class	Continuous-Sensor
Categories of Water	Fresh, Waste or Saline. See following table for typical applications:

Typical Liquid Products Monitored with Monitek Industrial Turbidimeters

Product	Color	Expected Turbidity (ppm)
Beer	Light Yellow to Brown	0-5
Wine (Chablis through Burgundy)	Clear to Dark Red	0-0.2 to 0-5
Champagne	Clear to Red	0-0.2 to 0-5
Brandy	Clear to Light Brown	0-0.2 to 0-4
Whiskey	Light Brown	0-5
Creme de Menthe	Green	0-5
Sugar Syrup	Clear to Brown	0-10
Apple Juice	Light Yellow	0-4
Concord Grape Juice	Dark Purple	0-20
Vegetable Oil	Light Yellow	0-10
Mineral Oil	Clear to Gray	0-10
Lubricating Oil	Clear to Brown	0-5
Cellulose Acetate	Clear	0-20
Resins	Various	0-20
Methylene Chloride	Clear	0-20
Pharmaceutical Solutions	Various	0-0.1 to 0-0.5
Potable Water	Clear	0-1

Principle of Operation

The liquid stream flows continuously through the piping and past a light source and light detector system. The intensity of light in the forward direction (direct light) is measured by one detector, while light scattered about 15° from the forward direction is measured by another detector. (Both the light source and detector are housed in the 215 or 210 Transmitter module). The 130 converter module computes the ratio of the electronic signals from the two detectors, and displays the result on a meter scale.

Table of Turbidimeter Parameters

Turbidimeter / Parameter	215	210
Light source	400-1000 nm Tungsten Lamp	400-1000 nm Tungsten Lamp
Range	0 to 0.1 0 to 100 0 to 1000	0 to 0.1 0 to 100 0 to 1000
Minimum Detectable Sensitivity, ppm	0.005	0.005
Liquid Stream Color Range	Deep Blue to Red	Deep Blue to Red
Pressure Rating, psig	150#	150#
Line Size	1.27 cm (0.5 inch)	1.27 to 15. 2 cm (1.5 to 6 inch)
Connections	1.27 cm npt. (0.5 inch)	150# Raised Face
Maximum Flow Rate, G.P.M.	-	100 to 1600

Interferences

Dissolved color interferences are eliminated by computing the ratio of forward scattered to direct light. Bubble-discriminating circuit rejects short, sharp pulses caused by bubbles to minimize this source of interference.

Multiparameter Capability

Oil in water

Sampling

Method: Continuous (flowing liquid stream)
Volume: Depends on flow rate (See Table of Turbidimeter Parameters)
Maximum Temperature Input: 0 to 121°C (0 to 250°F)
Collection Efficiency:
Maximum Number of Sample Sources: One

Performance

Accuracy:
Reproducibility:
Linearity: 1% full scale
Noise: <1% full scale on 0.1 ppm range
Lag Time:
Rise Time: 0.001 sec response time
Retention Time:
Fall Time:
Zero Drift: <1% full scale per day
Span Drift: <1% full scale per day

Operation

Ambient Temperature Range: -29° to 60°C (-20° to 140°F)
Temperature Compensation: None
Relative Humidity Range: 0 to 100%
Calibration: Transmitter contains a secondary light source. Activating a pushbutton on the converter control panel causes a fixed quantity of additional light intensity to be focused onto the scattered-light photodetector directly. This additional fixed quantity of light is intended to mimic a turbidity signal of known strength.
Procedure: Transmitter is installed in the liquid line to be sampled. Turbidity readings are read on the meter of the converter module.
Unattended Period: A month or more, depending on the application.
Maintenance: Change tungsten light source after two years (or longer).

Requirements

Power: 110 Vac/220 Vac; 50/60 Hz; 25 Watts
Weight: 13.6-22.6 kg (30-50 lb)
Dimensions: LT-130--35.6 cm H x 27.9 cm W x 12.7 cm D (14" H x 11" W x 5" D) See Table of Turbidimeter Parameters for Line Size dimensions of 215 and 210.

Features

Output: 0 to 10 Vdc (4 to 20 ma. optional). Displayed on 10.2 cm (4") meter.
Training:
Options: 215, 210 Transmitters:
(1) Alternate Body Materials (Bronze, cast iron, carbon steel, others)
(2) High temperature operation to +204°C (+400°F)
(3) Explosion proofing; light source in Class 1, Group D, Division 1 explosion-proof configuration.

References

(1) Manufacturer's brochure, "Monitek Industrial Turbidimeters", undated.
(2) Manufacturer's letter, December 28, 1972.
(3) Manufacturer's communication, April 6, 1973.

Cost

$2250 to $3425

Remarks

Above information taken from References 1, 2, 3.

Address

Monitor Technology, Inc.
303 Convention Way
Redwood City, CA 94063
(415) 365-6550

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

H2O-PHY
Field: TUR
Monitor Technology 5
April 1973

Turbidity in Water

Monitek Model 215/130 Slip-Stream Turbidimeter

Class	Continuous Sensor
Categories of Water	Fresh, Waste, Saline
Principle of Operation	An in-line or slip-stream flow of water continuously flows past a light source and detector system. The intensity of light in the forward direction is measured by one detector (direct light), light scattered about 15° from the forward direction is measured by another detector: Light source and detectors are mounted in the 215 transmitter module. The 130 module converter computes the ratio of the electronic signals from the two detectors, and displays the result on a meter scale. The meter reading is related to sample turbidity from calibration data.
Minimum Detectable Sensitivity	0.001 ppm
Range	0-0.1, 0.2, 0.5, 1, 2, 5, 10, 20, 50, 100 ppm
Interferences	Dissolved color and bubble interferences eliminated by use of ratio computation, and by electronic circuit which discriminates against short, sharp pulses caused by bubbles, respectively. Filters are included to eliminate stray light interference in the detectors.
Multiparameter Capability	None
Sampling	Method: Continuous (in-line, or slip-stream) Volume: Line pressure to 150 psi (through 8.89 cm, 3-1/2", DIA.) Maximum Temperature Input: 121°C (250°F) Collection Efficiency: Maximum Number of Sample Sources: One

Performance

Accuracy:
Reproducibility:
Linearity: 1% full scale
Noise:
Lag Time:
Rise Time: 0.001 sec
Retention Time:
Fall Time: 0.001 sec
Zero Drift:
Span Drift:

Operation

Ambient Temperature Range: -17.8° to 162°C (0 to 325°F)
Temperature Compensation:
Relative Humidity Range: 0 to 100%
Calibration: Dynamic: Manufacturer includes built-in calibration system to check electronics
Procedure: For built-in calibration, turn panel switch to calibrate position
Unattended Period: Indefinite for non-fouling liquids
Maintenance:

Requirements

Power: 110 Vac/220 Vac; 50/60 Hz; <50 Watts
Weight: 22.8 kg (50 lb)
Dimensions: Transmitter--14 cm x 63.5 cm x 8.9 cm (5-1/2" x 25" x 3-1/2")
Converter--35.6 cm x 28 cm x 12.7 cm (14" x 11" x 5")

Features

Output: 4 to 20 ma.; 0 to 10 Vdc
Training:
Options: (1) Cable length up to 61 meter (200 feet)
(2) Light source available in Class 1, Group D, Division 1 explosion-proof configuration

References

(1) Manufacturer's brochure, "Monitek Model 215/130 Slip-Stream Turbidimeter," undated.
(2) Manufacturer's letter dated December 28, 1972.
(3) Manufacturer's communication, April 6, 1973.

Cost

$2250

Remarks

Above information is taken from References 1, 2 and 3.

Address

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H20-PHY
Field: TUR
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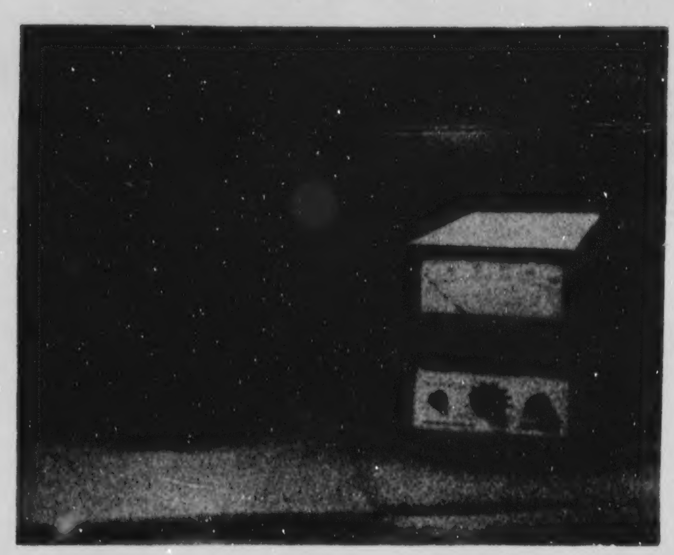
Turbidity

Model 350 Submersible Turbidimeter



Class	Continuous Sensor
Categories of Water	Fresh, Waste, Saline
Principle of Operation	Forward scatter ratio method using two separate light sources and detectors. The sources and detectors are sequentially switched and the two ratios of forward scattered light to unscattered light are calculated. Using these two ratios, an internal computer then generates the turbidity measurement which is read out on a meter. This computation also eliminates errors due to changes in light source and/or ambient light conditions. Remote/submersible operation is possible up to 3048 meters (100 feet). The submersible turbidimeter is intended for real-time monitoring.
Minimum Detectable Sensitivity	0.1 JTU
Range	Several: 0-5, 10, 20, 50, 100, 200, 500, and 1000 JTU
Interferences	More than 75-80% obscuration of submersed optical surfaces, and bubbles cannot be tolerated.
Multiparameter Capability	None
Sampling	Method: Submerge measuring head into water. Volume: Maximum Temperature Input: Collection Efficiency: Maximum Number of Sample Sources: One

Performance	Accuracy: 2% full scale Reproducibility: 1% full scale Linearity: 1% full scale Noise: 1% maximum (full scale) Lag Time: } 1 second data cycle Rise Time: } Retention Time: Fall Time: 1 second Zero Drift: <1% per day Span Drift: <1% per day
Operation	Ambient Temperature Range: -10°C to 100°C Temperature Compensation: None Relative Humidity Range: 0 to 100% Calibration: Static calibration using formazin or silica suspensions Procedure: See: "Standard Methods for the Examination of Water and Wastewater", 13th Edition, American Public Health Association, Washington, DC 20036 (1971), p 349. (Static methods) Unattended Period: >4 weeks; depending on severity of application Maintenance:
Requirements	Power: 110 V, 50-60 Hz, 25 watts Weight: 13.6 kg (30 lb) shipping weight Dimensions: Sensor head: 10 cm D x 25.4 cm L (4" x 10") Converter: 16.5 cm x 19 cm x 30.5 cm (6-1/2" x 7-1/2" x 12")
Features	Output: 0-10 Vdc, standard Training: None needed Options: Cable length: 7.6 to 61 meters (25 to 200 feet). Wetted parts on sensor head may be other than 315 stainless steel, quartz or neoprene.
References	(1) Manufacturer's Bulletin, 'Monitor Model 350 Submersible Turbidimeter", undated (2) Manufacturer's communication, October 18, 1972. (3) Manufacturer's communication, April 6, 1973.
Cost	Model 350 $2,650
Remarks	According to manufacturer, Model 350 compensates for source drift, liquid color, ambient light or window obscuration (up to 80%) effects in turbidity measurements. Forward scatter turbidimeters can have a higher signal output and can be more sensitive to larger particles. See: A.P. Black and S.A. Hannah, "Measurement of Low Turbidities", J.Am. Water Works Assoc., 57(7), p. 901 (1965). Above information taken from References 1, 2, 3.
Address	Monitor Technology, Inc. 303 Convention Way Redwood City, CA 94063 (415) 365-6550

Radiation
RAD

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FOR
RADIATION MONITORING IN AQUA-SYSTEMS

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RADIATION MONITORING IN AQUA-SYSTEMS

A. INTRODUCTION

There are many operations requiring the measurement of radioactivity in waters: industrial, medical, sanitary and public health. The most important of these stems from the need to assure that levels of activity are maintained below the limits set for human consumption. However, analyses are also involved in establishing acceptable radionuclide levels for agricultural and industrial uses; for effluent and process control; in the measurement of natural background radiation; in studies of radionuclide transfer in aquatic systems, and in tracer studies of flow systems. Environmental sampling may involve the collection of drinking water, industrial or municipal wastewaters, ground or surface waters, and rainwater or seawater.

Sometimes the measurement of gross activity with a suitable detector will suffice. More often than not, one or more specific nuclides are involved in the quantification, or a mixture of unknown composition requires qualitative as well as quantitative identification. The techniques used in identifying and measuring radionuclides are varied, and may include any or all of the following operations:

1) chemical separation
2) counting with instruments sensitive to a specific radiation
3) the use of absorbers or of spectrometers in an appropriately selected energy range.
4) use of a multiple measurement technique which can then be correlated with the isotopic decay pattern, the half-life (or half-lives, if decay products are also radioactive) or with some genetic parent-offspring relationship(s) in the observed decay.

In the routine monitoring of water quality, the three kinds of activity most commonly measured are alpha, beta and gamma radiation. Their salient characteristics and most frequently used instrumentation are listed in Table 1, together with commonly encountered units and terms. Other radiation species will be discussed briefly in section B. Absorption of Radiation in Water.

A more detailed treatment of the specific types of radiation and their measurement is available in Volume 3 (RADIATION) of this survey (Ref. 1c). For an excellent general reference, the reader may consult Glasstone's Sourcebook on Atomic Energy (Ref. 2a).

The monographs of the NAS Subcommittee on Radiochemistry, dealing with the radiochemistry of individual elements (Ref. 3), should be consulted as a basic reference to radiochemical analysis.

Chemical Abstracts (C.A.) and Nuclear Science Abstracts (N.S.A.) provide current abstracts in the field of nuclear chemistry. Analytical Chemistry publishes a biennial summary of recent publications in nuclear chemistry and nucleonics.

Information on the sampling, preservation and detection of activity at the extremely low concentrations of radionuclides present in environmental waters may be found in the ASTM Annual Book of Stds., Part 31 (Ref. 4) and in Standard Methods (14th edition), pp. 631-682 (Ref. 5).

Specific radionuclide intake guides and their permissible concentrations in water are given in Table 6 (Criteria). Maximum permissible concentrations of radionuclides in air and water are listed in Table 7. A more complete listing is provided in the CRC Handbook (Ref. 6), pp. 617-631, inclusive.

The radiation chapter in Volume 4 (BIOMEDICAL) of this series (Ref. 1d) contains a more in-depth discussion of radiation in biological systems.

Other references listed at the end of this chapter cover such special areas as separation methods for low-level activity radionuclides, rapid techniques for separation, measurement and detection, computer methods and counting (Ref. 3b). For a general discussion of radioactive nuclides in water, see Chapter XIV of the ASTM Manual on Water (Ref. 7). An overall survey of radioactive elements is provided by Haissinski and Adloff (Ref. 64). References 65 to 67 inclusive are standard monographs dealing with the measurement of radioactivity. For textbooks dealing with nuclear chemistry, see Friedlander et al., and Duncan (Refs. 34 and 35). An excellent treatment of the radiation chemistry of water is found in the monograph of the Draganićs (Ref. 9).

1. Historical

Prior to 1945, the question of radioactive contamination of waters was, with the exception of perhaps some known existing radioactive springs, purely academic. Even the latter evinced little concern as a potential public health hazard. In fact, historically radioactive springs had been exploited for their supposed healing properties. With the first successful detonation of a nuclear weapon,[a]

---

[a] July 16, 1945, Alamogordo, N.M. (Ref. 7)

TABLE 1
Types of Radiation, Instrumentation and Units Encountered in the Routine Radiation Monitoring of Water

A. Radiation	Symbol	Sources and Characteristics	Instrumentation
alpha particles[a]	He^{++}, α	Highly ionizing, positively charged particles emitted by many naturally occurring radionuclides. Discrete energies. Short range. Atomic mass 4.	Ionization chambers, low voltage proportional counters ZnS Scintillators
beta particles[a]	e^-, e^+, $\beta^\pm$	Electrons/positrons emitted by all fission products and most thermal neutron activation products. Continuous distribution of energies from zero to characteristic maximum values. More penetrating than α-particles (for energies > 0.1 MeV) Mass ~ (1/1850)H.	Gas counters in Geiger-Müller and proportional voltage regions. Solid and liquid scintillation counters. Photographic film.
gamma and x-rays[b]	γ X	Relatively penetrating electromagnetic radiation. Interacts with matter via the photoelectric effect, pair production or Compton scattering, exhibiting characteristic peak energies in the first two instances. Absorption follows Beer's Law: $I = I_o e^{-\mu x}$ Where I = initial intensity I_o = intensity after traversing absorber of thickness x(cm) μ = attenuation coefficient (absorption coefficient) of the absorber	Gamma-ray spectrometers Large crystal scintillators (eg NaI(Tl); > 0.1 MeV) Thin crystal scintillators (0.02 = 0.1 MeV) Ge-Li Detectors Gas proportional counters (Xenon for ~ 0.01 MeV X-rays)

a) see Table 2
b) see Table 4

TABLE 1 (cont.)

B. Terms and Units

Classification	Name	Unit(s)	Symbol	Definition
Radioactivity	activity	Curie	Ci	Number of nuclear disintegrations occurring/unit of time: 1Ci = 3.7×10^{10} transformations/second.
Radiation	roentgen	roentgen	R	Amount of ionization produced in a unit mass of air under standard conditions: 1R = 2.58×10^{-4} coulombs/Kg = 87.6 ergs/gm
Dose	radiation-absorbed-dose	rad	rad	1 rad = absorbed dose of 100 ergs/gm = 0.01 joules/Kg
Energy	electron volt	electron volt	eV	Energy acquired by a unit charged particle when it falls through a potential of one volt: 1 ev = 1.60×10^{-12} ergs
Radiation Yield	yield	molecules/ 100 eV/g	G	G = The number of molecules decomposed/100 eV deposited/g
Biological Dose equivalents	roentgen equivalent man	rem	rem	The quantity of radiation which produces the same biological damage as that produced by 1 rad of X- or γ-rays: 1 rem = Dose (rads) x RBE
	relative biological effectiveness	———	RBE	Ratio of the dose of 200 keV x-rays to the dose of the given radiation producing the same biological effect: RBE-dose (rems) = Dose (rads) xQF[a]
	dose equivalent	rems	DE	DE (rems) = Dose (rads) x QF
	quality factor	--	QF[a,b]	Assigned value related to RBE and LET
Energy	linear energy transfer stopping power	keV/μ	LET[b]	Energy released or deposited by the radiation/unit distance LET (keV/micron) = stopping power

a) See Table 1A
b) See Table 1B

TABLE 1A

Quality Factor Values for Various Radiations

Radiation	QF
Gamma-rays from radium in equilibrium with its decay products (filtered by 0.5 mm platinum)	1
X-rays	1
Beta-rays and electrons	1
Thermal neutrons	3
Fast neutrons	10
Protons	10
Alpha-rays	10
Heavy ions	20

TABLE 1B

Relationship Between Quality Factor and Linear Energy Transfer

LET keV per micron in water	QF
3.5 or less	1
3.5-7.0	1-2
7.0-23	2-5
23-53	5-10
53-175	10-20

all this was changed. Radioactive fallout from this test was responsible for extensive fogging of photographic films via the radionuclide contamination of the processing water and subsequently the film wrappers (Ref. 7).[a]

Studies of the in vivo and in vitro effects of radiation appeared in great numbers after August 1945.[c] As a result of these studies and the work of numerous committees (Appendix I) concerned with radiation protection of the public and of personnel employed in the developing fields of nuclear medicine and reactor technology, certain criteria and standards have evolved. The biological aspects of radiation are discussed in greater detail in LBL-1, Volume 4, BIOMEDICAL (Ref. 1d).

2. Sources

Radioactivity in water and waste water now derives from both natural and artificial sources. The latter category includes fallout from nuclear weapons tests, wastes and emissions from nuclear reactors and high energy accelerators and from the medical and industrial use of radioisotopes. In general, the natural background activity is low, contributing less than picocurie (pCi) amounts per liter of α-activity to surface waters and about ten times as much β-activity. However, there are some exceptions: natural radioactivity such as radium in some groundwater supplies, and uranium plus daughters from a number of mining operations (uranium, phosphate, vanadium, etc.) are considered "a significant source of radiation exposure to the US population" according to Dr. James Channell, Chief of the EPA Hazardous Materials Branch.[a] Nevertheless it is the artificial sources of radioactive contamination which are of greatest concern to environmental and public health agencies. Here the chief pollutants derive from the production and use of artificial radionuclides in a variety of medical, research, industrial and military applications as noted above. Of these sources, the greatest future concern will in all likelihood center about the nuclear power industry: its reactors and fuel processing plants, waste storage and disposal facilities, as it expands to meet our energy needs. (Ref. 8).

3. Nature of Radioactivity

Radioactivity may be defined as the spontaneous emission of radiation from unstable atomic nuclei. Early workers classified this radiation into three types (α,β,γ) on the basis of the direction of deflection of emitted rays by an applied magnetic field, and by the ability of these radiations to penetrate matter. Alpha (α) rays were identified as high speed helium nuclei by these workers, beta (β) radiations, as electrons also moving at very high speeds. Gamma (γ) rays were characterized as highly penetrating electromagnetic radiations very similar to the X-rays produced in cathode ray tubes.[b]

The findings of early investigators of the relative penetrating powers (range) of α, β and γ radiations are depicted graphically in Figure 1. Thus, while α-particles are completely stopped by a few sheets of paper and β's absorbed by a few millimeters of aluminum, sufficiently energetic γ radiations may not be absorbed completely, even by several centimeters of lead.

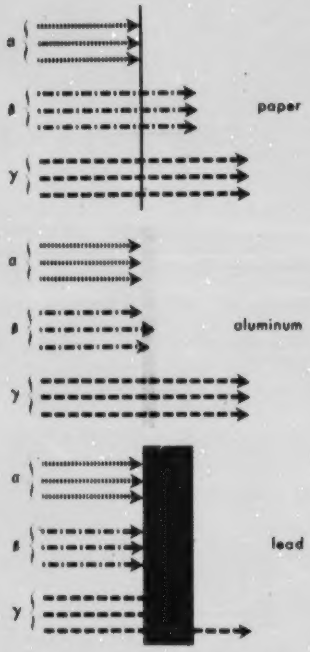

FIGURE 1. Relative penetrating power of alpha, beta, and gamma radiation (Ref. 71).

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[a] Henri Becquerel (1895) first observed the blackening effect of potassium uranyl sulfate on photographic film wrapped in black paper, and deduced from this that the salt was emitting a penetrating type of radiation (later known as γ-radiation) (Ref. 2b).

[b] For further historical details see Refs. 2b and 7. See also the 1975 World Almanac.

---

[a] Private Communication (3/2/76)

[b] Some years later (1932), positrons, or positive electrons (β^+) were observed by C. D. Anderson in the cosmic ray tracks of a Wilson Cloud Chamber.

The *range* of a particle in a medium is inversely related to the *stopping power* of the medium, and is governed by two factors: 1) its initial maximum energy and 2) the density of the medium. Thus, for a given particle energy, the range in water ($d_{H_2O} = 1$) may, to a first approximation, be expected to be 2 to 3 times its range in aluminum ($d_{Al} \simeq 2.7$). On the other hand, lead ($d_{Pb} \simeq 11.3$) has much greater stopping power than either of the above substances - a characteristic which makes it particularly useful in shielding against highly penetrating gamma radiation. In Table 2 the ranges of α- and β-emissions in air (cm) and water (microns: $1\mu = 10^{-4}$cm) are compared. The last column gives LET (linear energy transfer) data in water. It is clear that the relatively heavy, doubly charged alphas lose energy very rapidly to the medium, as was also shown graphically in Figure 1. This is an important consideration in the selection of appropriate detection geometry.

3.1 General Principles

The spontaneous emission of high energy radiation from an atomic nucleus results in its transformation or rearrangement to a more stable (i.e., lower energy) nuclear configuration. The rate at which this radiation is emitted is a characteristic specific of the particular radionuclide in question. It is often expressed in terms of the *half-life* --the time required for one-half of the unstable nuclei to complete their decomposition.

If a radioactive substance such as uranium-238 is separated from other radioactive material and its activity measured, the decay rate will be found to follow an exponential law. Thus, at any instant, the decay rate will be proportional to activity I at that instant, and may be expressed by equation (1):

$$-dI/dt = \lambda I \qquad (1)$$

where λ, the *decay constant*, is characteristic for the given nuclide.[a] On integration, equation (2) is obtained:

$$I = I_0 e^{-\lambda t} \qquad (2)$$

where I_0 is the initial activity measured. Making the reasonable assumption that the activity at any instant is proportional to the number (n) of intact atoms remaining, it follows that:

$$n = n_0 e^{-\lambda t} \qquad (3)$$

where n and n_0 represent the final and initial numbers of active atoms remaining. Thus it is clear that the life of any particular atom can vary all the way from zero to infinity, the gradual decay of the element in question being a measure of its nuclear stability.

A useful concept is that of the *average life* for a large aggregate of such atoms. It may be calculated from the following considerations: Since the activity I is proportional to the number of intact atoms, n, equation (1) may be expressed as

$$-dn/dt = \lambda n. \qquad (4)$$

Substituting the value of n from equation (3) we obtain the expression

$$-dn = \lambda n_0 e^{-\lambda t} dt \qquad (5)$$

For the interval between t and $t + dt$, the number of atoms disintegrating will be dn. For dt vanishingly small, dn may be treated as the number disintegrating at time t. At any instant in time t it is clear that dn

---

[a] The brief mathematical treatment which follows may be omitted and the text continued from Section 3.2. Energy Characteristics, which follows.

TABLE 2. Range and LET Values for Alpha and Beta Particles (Ref. 63)

Isotopes	Energy of alpha or beta particles, meV	Mean range in air 15 C,760 mm Hg, cm	Mean range in water, microns	Average LET in water, keV/micron
radium-226	4.795	3.3	33	145
polonium-210	5.30	3.8	38.9	136
radon-222	5.49	4.0	41.1	134
beta particle	1	.405	4100	0.24
beta particle	3	1400	15000	0.20
beta particle	10	4200	52000	0.19

represents[a] the number of atoms with a life expectancy t subsequent to that instant. By multiplying every possible life period t (from zero to infinity) by the number of atoms, dn , having that life expectancy and dividing the sum of these products by n_0, the initial (total) number of atoms present at t_0, one obtains the average life, τ(tau).

$$\tau = \int_0^\infty \frac{t\,dn}{n_0} = \int_0^\infty t\lambda e^{-\lambda t}\,dt = \frac{1}{\lambda} \qquad (6)$$

Thus the *average life* of the radioactive atom is the reciprocal of its radioactive constant, λ, and is a measure of the *mean life expectancy* of the atoms remaining.

The half-life (T = t/2) mentioned previously is an important quantity in that it is a measure of the time required to reduce the radioactivity at any instant to one half its value at that instant. It may be calculated from equation (3) above by letting $n = \frac{1}{2} n_0$. Then

$$\tfrac{1}{2}n_0 = n_0\ e^{-\lambda T} \qquad (7)$$

and

$$T = \ln 2/\lambda = 0.693/\lambda. \qquad (8)$$

TABLE 3. Radioactivity Calculations and Definitions (Ref. 24)

Decay rate vs. number of atoms and half-life:

$$\frac{dN}{dt} = \frac{0.693N}{t_{1/2}} \qquad \text{(a)}$$

Molar concentration vs. radioactivity concentration:

$$M = 8.9 \times 10^{-17}\, C t_{1/2} \qquad \text{(b)}$$

Decay of radionuclides:

$$C_1 = C_0 e^{-0.693t/t_{1/2}} \qquad \text{(c)}$$

Radioactivity concentration from count rate:

$$C = (A - B)(VYE\, e^{-0.693t/t_{1/2}})^{-1} \qquad \text{(d)}$$

Counting error:

$$s = \left(\frac{A}{t_A} + \frac{B}{t_B}\right)^{0.5} \qquad \text{(e)}$$

Minimum detectable concentration (8):

$$C_{min} = 3\left(\frac{B}{t_A}\right)^{0.5} (VYE\, e^{-0.693t/t_{1/2}})^{-1} \qquad \text{(f)}$$

Definitions

dN/dt	disintegration rate, atoms/min
N	number of atoms
$t_{1/2}$	half-life, min
M	molarity, mole/liter
C	radioactivity concentration, μCi/ml
C_1	radioactivity concentration at time t, μCi/ml
C_0	initial radioactivity concentration, μCi/ml
C_{min}	minimum concentration attributed to radioactivity in sample, μCi/ml
t	interval, min
V	sample aliquot, ml
Y	carrier yield, mg recovered/mg added
E	overall counter efficiency, count/min per μCi
A	count rate, count/min
B	background count rate, count/min
t_A	counting period, min
t_B	background counting period, min
s	counting error, 1 standard deviation, count/min

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[a] Without regard to its algebraic sign in equation (5).

Some of the more common calculations involved in the determination of radionuclides in water, and deriving from the preceding analysis, are given in Table 3.

3.2. Energy Characteristics

Nuclear disintegrations involve much greater energy releases than ordinarily observed in chemical change. The magnitudes of these differences between chemical and nuclear transformations are the order of 10^6. In the case of α-particles or γ-radiation this energy is removed largely by the emitted radiation itself. Beta emission differs in that the total energy available is distributed between a β-particle and a neutrino (not ordinarily observed). Since the energy distribution between these two particles may vary for each disintegration, the energy of a particular β-particle may range all the way from zero to maximum energy, with an average value of approximately one third of the total. Thus, β-radiation has a continuous spectrum, as opposed to the sharper line spectra exhibited by α- and γ-radiation.

The most commonly encountered unit of energy in radioactivity is the *electron volt* (eV). This is defined as the energy gained by an electron in passing through a potential difference of 1 volt (see Table 1, under B). Alpha particles have energies of a few million eV (MeV), while β- and γ-radiation may range from zero to a few MeV, but are most frequently found in the 100 to 500 keV‡ range.

As radiation travels through matter, energy transfer occurs. The quantity of energy transferred is a function of the medium as well as the particle energy. This is well illustrated for α and β-particles in air and water in Table 2.

In the absorption of γ-radiation, photon energy is converted to the kinetic energy of electrons. Gamma radiation intensity is quantified in terms of the thickness of absorber required to reduce its intensity by some fraction. Thus, the terms *half value layer* or *half thickness* define the thickness of absorber required to reduce the radiation intensity to one-half of the initial value (Table 4).

For alpha and beta radiation (both involving charged particles) interaction is primarily electrostatic in nature with energy being transferred to the electrons of the material as its electrons come within the electrostatic sphere of influence of the particles. There is, however, considerable quantitative difference in their interaction with matter, since the much heavier α-particles are slower moving and interact with many more electrons per unit of path length. In the case of the neutral gamma radiation, interaction is essentially statistical in nature, with no energy transfer occurring until a photon interacts with an electron, thereby relinquishing all or a large part of its energy by transfer. Unlike alpha and beta radiation, gamma radiation does not have a specific range -- it is simply reduced in intensity on passage through matter (see Table 1, under A).

B. ABSORPTION OF RADIATION IN WATER

As a consequence of the interaction of any of these three radiations with matter energy is transferred to electrons, resulting in ionization and/or molecular excitation. These interactions produce secondary changes such as the darkening of a photographic film or the initiation of some other chemical (or biochemical) change. In the biochemical instance the interaction may have biological consequences. These biological effects are dose-dependent; that is, they are a function of the energy absorbed. The unit of energy absorption, or *rad*, is quantitatively equivalent to the absorption of 100 ergs/gram. For in vitro aqueous systems this same dose dependence exists. However, *radiation yields* are generally expressed in terms of number of molecules changed/100 eV of radiation absorbed.

1. Gamma and X-Radiation (Photons)

The manner in which photons lose energy to water is dependent on the magnitude of their incident energy. Below 0.01 MeV the *photoelectric effect* dominates, e.g., complete transfer of energy to the ejected electron occurs. However, for energies between a few

TABLE 4. Half-thickness Values for γ Radiation (Ref. 63)

		Half-value layer, cm			
Isotope	γ energy	Water	Aluminum	Concrete	Lead
^{137}Cs	0.66	8.1	3.4	3.8	0.57
^{60}Co	1.25(mean)	11	4.6	5.2	1.06

---

‡1 keV = 1000 eV

keV and a few MeV another process, known as the Compton Effect, predominates. In this instance only a part of the photon energy is transferred to an electron and the depleted photon continues on a deviated path. Another process, *pair production,* is not generally significant in aqueous radiation-chemical processes, but can occur with photon energies > 1 MeV. Where sufficiently high photon energies are involved all three processes may occur simultaneously in water. The probability that any given photon will interact by one of these processes during its passage through water may be expressed in terms of the Beer-Lambert absorption expression:

$$I = I_0 \, e^{-\mu x}. \qquad (9)$$

Here, I_0 is the initial radiation intensity (ergs/square cm/sec.), I, the intensity of the transmitted radiation through x centimeters of water, and μ is the total linear absorption coefficient in reciprocal centimeters (cm^{-1}), where

$$\mu \text{ total} = \mu \text{ photoelectric} + \mu \text{ Compton}$$
$$+ \mu \text{ pair production}. \qquad (10)$$

By substitution of the appropriate μ values for water into the Beer-Lambert equation, the thickness x (cm) required to absorb a specific fraction of the incident radiation may be readily calculated. Thus, 1 MeV γ-radiation loses only a small fraction of its intensity in traversing several centimeters of water; by contrast, *soft X-rays* with energies in the lower keV range are absorbed by a few millimeters of water.

Figure 2 is a plot of atomic absorption coefficients against photon energies in water with a breakdown of the contributions of the three components discussed as a function of energy. For a more detailed discussion of γ- and x-radiation, the reader is referred to LBL-1 Volume 3, RADIATION (Ref. 1c).

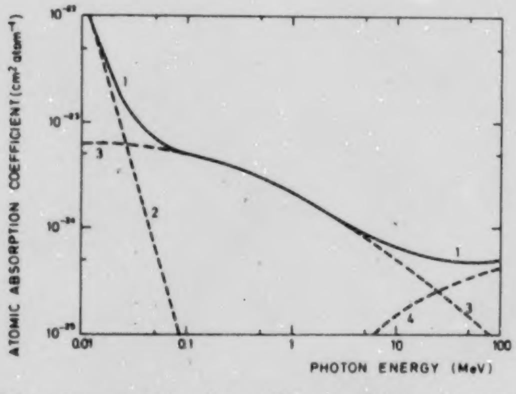

FIGURE 2. Atomic absorption coefficients for water: the total absorption coefficient (1), the photoelectric coefficient (2), the total Compton coefficient (3), and the pair production coefficient (4). (Ref. 9, p. 25).

2. Electrons

An electron traversing a layer of water of thickness x will lose its energy much more gradually than does a photon, ionizing a large number of molecules along the way. The average distance traversed by the electron will depend on its initial velocity and is of the order of thousands of angstroms. Figure 3 illustrates the dose-depth relationships for electrons in water.

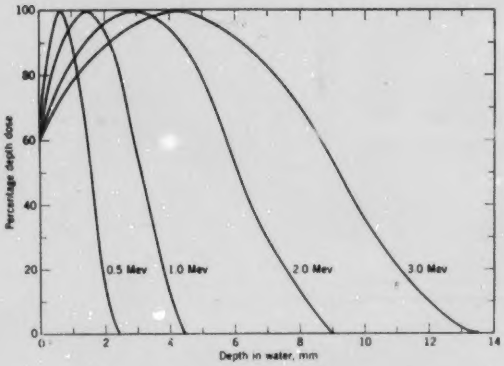

FIGURE 3. Dose-depth curve in water for electrons (Ref. 63, p. 55).

The sudden loss of energy when a very fast electron approaches the positively charged nucleus of an atom results in a radiation phenomenon known as *bremsstrahlung.* However, this is uncommon under the usual radiation conditions in aqueous solutions since energies are generally < 5 MeV and water is a low Z medium.†

Secondary electrons produced in the primary ionization processes may lose energy in one of a number of ways; namely, by the
1) excitation of molecular species,
2) neutralization of positive species present,
3) attachment of electrons to neutral molecules,
4) hydration and polarization of the medium.
When electron capture by a neutral molecule or a positive ion occurs, the product may dissociate or fragment.

Electrons may be classified into the four following groups according to their energies:

a) Fast: E $\gtrsim$ 100 eV. These excite and ionize the aqueous medium to optically "allowed" states, primarily; in hard collisions they may produce fast secondary (δ) electrons on occasion.

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† Z = nuclear charge

b) Slow: 100 eV > E > E_0 (threshold electronic excitation). While these electrons excite and ionize to allowed states, they may also do so to so-called "forbidden" states by means of "electron exchange" processes.

c) Subexcitation Electrons: $E_0 > E > kT$. These species may induce vibrational and/or rotational excitations. They may also neutralize positive ions and, more importantly, cause *indirect* excitation via temporary negative ion production.

d) Thermal Electrons: $E \sim kT$. These low energy electrons may serve to neutralize charge, may be attached to neutral species dissociatively or non-dissociatively, or effect polarization of the aqueous medium.

In the radiation chemistry of water the chief concern is with energy loss via *inelastic collisions*: this is the principle process in the electron energy range $E \geqslant 100$ eV. For this range Allen has derived a simple form of the Bethe-Askin equation for electron energy loss (Ref. 9)

$$-\frac{dE}{dx} = \frac{1.019}{E} \log \frac{E}{56.6} \qquad (11)$$

where E is in electron volts (eV) and $-\frac{dE}{dx}$ in eV/angstrom. Using this expression one obtains $-\frac{dE}{dx}$ values which go from 0.22 eVA^{-1} for 10 keV electrons down to 0.02 eV A^{-1} for 400 keV, after which energy loss remains essentially constant (except for the minimum of 0.018 eVA^{-1} attained between 1 and 2 MeV) up to 5 MeV.

3. Heavy Charged Particles

In addition to α-particles *(helions)*, protons and deuterons also are in this category. As with β-particles, these transfer energy to the aqueous medium by ionizing and/or exciting water molecules in successive collisions until the species are slowed down sufficiently to be neutralized by electrons. Again, since only inelastic collisions are of interest in the usual radiation chemical studies of water, equation (12) suffices to calculate the energy loss:

$$-\frac{dE}{dx} = \frac{4\pi Z^2 e^4}{m_o V^2} NZ \left[\log \frac{2\, m_o V^2}{(1-\beta^2)} - \beta^2 \right] \qquad (12)$$

where $-\frac{dE}{dx}$ is expressed in ergs/cm and the other quantities are as defined in the Bethe-Askin equation 11(Ref. 9, p. 27). From equation 12 it is seen that energy loss varies inversely as the square of the velocity, and directly as the particle charge. Thus, for the same initial energies the helion will have greater energy loss than the deuteron because of its lesser velocity and greater charge.

4. Neutrons

Unlike charged particles, the primary interaction of neutrons with water involves nuclei, rather than electrons, the neutrons giving up their energy in elastic collisions with nuclei (for energies > kT). Here, the smaller the mass of the target nucleus, the larger the energy loss. Thus in water a hydrogen nucleus will take up about half the neutron energy, lose its electron, and produce a proton in the process. Thermal neutrons are usually captured by the hydrogen nucleus in water, giving rise to the nuclear reaction $^1H(n,\gamma)^2H$ with emission of 2.2 MeV gamma radiation. Under the usual conditions obtaining in water, the corresponding (n,γ) reaction with oxygen may be neglected.

C. RATIONALE FOR RADIATION MONITORING OF WATER

Water is of prime importance to the survival of bio-systems - the latter being themselves largely aqueous suspensions and solutions of essential substances. Thus, the radiation chemistry of water can furnish valuable insights into questions concerning chemical processes which may occur when living systems are irradiated.

The peptide bond and other fundamental groupings in biological systems are particularly sensitive to radiation. This sensitivity has been used to advantage in radiation therapy, in which more rapidly multiplying cancer cells are preferentially destroyed by the use of large doses of radiation. Unfortunately, selectivity of this process is limited, and healthy cells are destroyed along with the malignant variety. Excessive exposure to radiation may result in a broad spectrum of physiological responses, varying all the way from skin lesions to nausea, anemia, inhibition of the immune mechanism which provides resistance to disease and infections, or to death itself. In lower doses, radiation may result in less obvious changes *(mutations)* with the concomitant risk of genetic consequences to progeny, or of the induction of delayed cancer. Much remains to be learned about the cumulative effects of low doses of radiation. However, in the context of current knowledge, the ICRP[a] and NCRP[b] have established certain acceptable risk levels (Ref. 10,11). However, these criteria are strictly advisory. Maximum permissible concentrations (MPC) are set by the Nuclear Regulatory Commission (NRC) for their licensees, and by the Energy Research and Development Administration (ERDA) for their facilities. Non-occupational Standards fall within the purview of the EPA (see below).

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[a] International Commission on Radiological Protection.

[b] National Council on Radiation Protection and Measurements.

As a result of the sensitivity of biological systems to ionizing radiation, the presence of radionuclides in air and water, as well as in foods and other commercial products, must be rigidly monitored and regulated. Thus, since radionuclides differ in their metabolic, chemical and physical characteristics, standards of exposure must be established which guarantee that no organ will receive more than the specified acceptable risk exposure. These maximum permissible concentrations (MPC) are now set by the Division of Criteria and Standards, Office of Radiation Programs (ORP), Environmental Protection Agency (EPA). A further discussion of these standards and criteria, and of the most recent recommendations for changes in drinking water standards proposed and promulgated by the Environmental Protection Agency (EPA), will be presented later in this chapter.

1. Radiation Monitoring: Agencies and Systems

In conjunction with their overall water quality monitoring activities, a number of agencies including the EPA, U. S. Geological Survey (USGS), and others - federal, state and local -- conduct extensive sampling and analysis programs for the radiation monitoring of ground and surface waters as well as treated waters. Generally measured in these surveillance programs are: gross α-and β-activities plus specific radionuclides such as Ra^{226}, Sr^{90}, I^{131}, and tritium.

One of the most extensive surveillance programs is the Environmental Radiation Ambient Monitoring System (ERAMS) operated by the EPA. It is the successor to the former Radiation Alert Network (RAN) with stations scattered throughout the U. S., including Alaska and Hawaii (Fig. 4). With increased interest in tritium releases from nuclear facilities with their potential for long-term accumulation in the environment, the Tritium Surveillance System (TSS), first incorporated into RAN is also a part of the restructured ERAMS. Typical quarterly data obtained for tritium in drinking water is shown in Table 5.

The following excerpts, taken from the June 1975 ORP Report 1(Ref.12a), details current EPA monitoring activities related to water quality.

> "The U.S. Environmental Protection Agency's Office of Radiation Programs (ORP) has restructured previously operating radiation monitoring networks

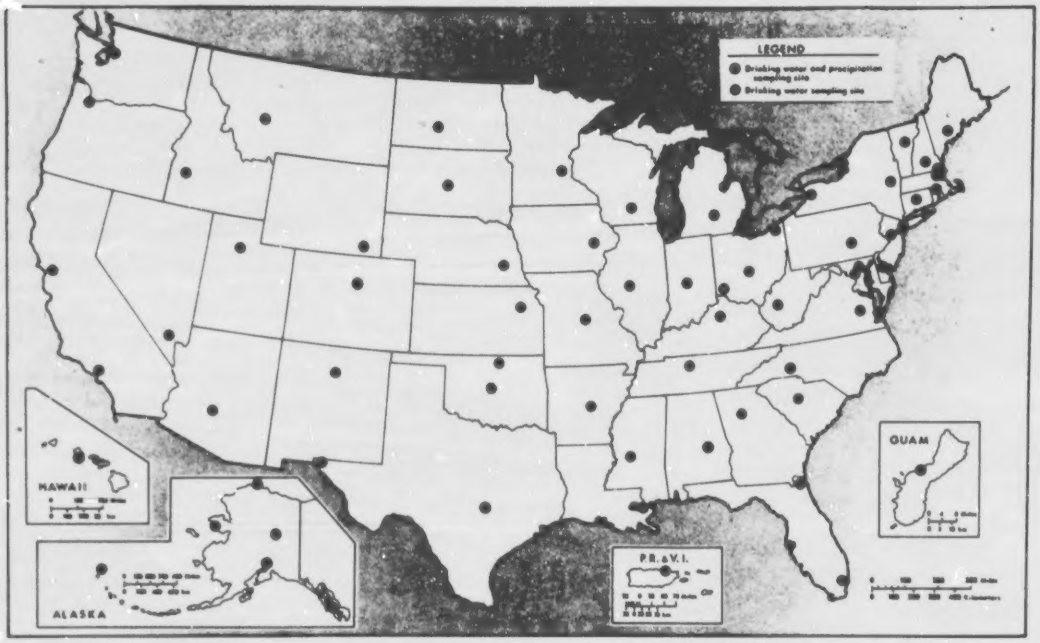
LEGEND
● Drinking water and precipitation sampling site
● Drinking water sampling site
HAWAII
ALASKA
GUAM
P.R. & V.I.

FIGURE 4. Drinking water and precipitation sampling locations for tritium surveillance system (Ref. 53, p. 16).

TABLE 5. Drinking Water Tritium Concentration (nCi/1) (Ref. 12a)

January - March 1975

Location	Date Sample Collected	2 Sigma Counting Error
AK:Anchorage	011475	0.5±0.2
Fairbanks	012475	0.4±0.2
AL:Dothan	012375	0.0±0.2
Montgomery	010275	ND
Muscle Shoals	011775	0.2±0.2
AR:Little Rock	010275	ND
CA:Berkeley	010275	0.0±0.2
Los Angeles	010275	ND
CO:Denver	011675	0.5±0.2
Platteville	011675	0.6±0.2
CT:Hartford	010375	0.0±0.2
CZ:Ancon	020375	ND
DC:Washington	020875	ND
DE:Wilmington	010675	ND
FL:Miami	010275	ND
Tampa	012175	ND
GA:Baxley	010975	0.0±0.2
Savannah	012775	2.3±0.2
HI:Honolulu	011475	0.0±0.2
IA:Cedar Rapids	010375	0.2±0.2
ID:Boise	010375	ND
Idaho Falls	010675	0.4±0.2
IL:Morris	011175	0.0±0.2
Chicago	011175	0.3±0.2
KS:Topeka	010275	0.2±0.2
LA:New Orleans	012275	0.2±0.2
MA:Lawrence	010275	ND
Rowe	012375	ND
MD:Baltimore	010875	0.2±0.2
Conowingo	010775	0.2±0.2
ME:Augusta	010275	ND
MI:Detroit	010775	0.4±0.2
Grand Rapids	010875	0.3±0.2
MN:Minneapolis	010775	0.4±0.2
Red Wing	010675	0.0±0.2
MO:Jefferson City	010875	0.0±0.2
MS:Jackson	010375	ND
MT:Helena	010375	0.3±0.2
NC:Charlotte	010675	0.3±0.2
Wilmington	031075	0.2±0.2
ND:Bismarck	010275	0.5±0.2
NE:Lincoln	011575	ND
NH:Concord	010275	ND
NJ:Trenton	010675	0.2±0.2
Waretown	010775	0.0±0.2
NM:Santa Fe	NS	
NV:Las Vegas	010275	0.7±0.2
NY:Albany	010675	ND
Buffalo	010275	0.3±0.2
New York	NS	
Syracuse	030975	0.5±0.2
OH:Cincinnati	010275	0.2±0.2
Columbus*		
East Liverpool	021975	ND
Painesville	010275	0.4±0.2
Toledo*		
OK:Oklahoma City	NS	
OR:Portland	010775	0.0±0.2
PA:Columbia	010775	0.2±0.2
Harrisburg	010875	0.2±0.2
Pittsburgh	011675	ND
PR:San Juan	011575	0.0±0.2
RI:Providence	010375	ND
SC:Anderson	012975	0.3±0.2
Columbia	010275	0.3±0.2
Hartsville	011775	0.2±0.2
Seneca	012975	0.3±0.2
TN:Chattanooga	010275	0.4±0.2
Knoxville	010275	0.3±0.2
TX:Austin	010275	ND
VA:Doswell	011475	ND
Lynchburg	010775	0.2±0.2
Norfolk	010375	ND
WA:Richland	010675	0.3±0.2
Seattle	010375	ND
WI:Genoa	011075	0.0±0.2
Madison	010975	ND
Network Average		0.23

ND - Not detectable.
NS - No sample.
* Newly established sampling sites. Data will appear in future issues.

into a single radiation monitoring system which is more responsive to current and projected sources of environmental radiation.

This restructuring consists mainly of changing the environmental radioisotope inventory which is monitored and realigning nationwide sampling locations to more closely coincide with the sources of such radiation.

"The initiation of the ERAMS was necessary in maintaining relevancy in ORP environmental radiation monitoring capability (nation-wide atmospheric fallout levels are declining while stationary radiation sources such as nuclear power reactors are increasing). Our previous monitoring program has been restructured to coincide with the change in potential environmental insult.

"The report series is compiled and distributed by the Office of Radiation Programs' Eastern Environmental Radiation Facility (EERF), Montgomery, Alabama.

SECTION II. Water Program [a]

"The ERAMS Surface and Drinking Water sampling activities are an expansion of the previous Tritium Surveillance System which was operated by the Office of Radiation Programs from 1970 through June 1973.

Surface Water

"Surface Water monitoring consists of 55 quarterly surface water samples taken downstream from nuclear facilities or at a background station. The location of the sampling sites was based on all nuclear facilities that were operating, being constructed, or planned through 1976. Tritium analyses are performed quarterly and gamma scans annually.

Drinking Water

"Drinking Water monitoring consists of 77 quarterly drinking water samples taken from major population centers and selected nuclear facility environs. The analyses include (a) tritium on a quarterly basis, (b) gamma scan, gross alpha and gross beta radioactive measurements annually with radium-226 and strontium-90 measurements if the gross alpha or gross beta radioactivity exceed 3 or 10 pCi/liter, respectively, and (c) an annual composite for plutonium-238, -239, uranium-234, -235, and -238, on 21 selected sampling locations.

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[a] Excerpts from ORP Report 1 (Ref.12a)cont.

"The analyses performed for the Drinking Water are currently being evaluated with respect to the Safe Drinking Water Act of 1974 and will be expanded to meet requirements of that legislation. Those analyses which may be added include strontium-89, radium-226, cesium-134 and cesium-137. Detection limits may also be altered to coincide with the Safe Drinking Water Act of 1974.

"The results of tritium in drinking water analyses for July 1974 to March 1975 are shown in Tables 18-20[a].

Interstate Carrier Drinking Water Analysis Program 1972

"The routine surveillance of finished drinking water from public drinking water supplies is a project of the Office of Water Program Operations of the Environmental Protection Agency (EPA), in partial fulfillment of the requirements as set forth in Subpart J of the Interstate Quarantine Regulation most commonly referred to as the Public Health Service Drinking Water Standards. The basic network for this activity is the approximately 700 water supplies (serving over half of the U. S. population with access to public water systems) which provide water for use by interstate carriers. Laboratory support is provided by the Eastern Environmental Radiation Facility and the Office of Radiation Programs -- Las Vegas Facility. All samples were taken either as a single grab sample or composite samples taken over 12 to 14 days. In many cases where a water system received raw water from more than one source, the finished drinking water derived from each source has been examined.

"The standards provide for the approval of water supplies, based on their radionuclide content, when the water does not contain more than 3 pCi/liter of radium-226 nor 10 pCi/liter of strontium-90. In the absence of strontium-90 and alpha emitters, the water supply is acceptable when the gross beta concentration does not exceed 1000 pCi/liter."

The most recent data from this program was published in the July 1976 issue of Radiation Data and Reports (No. 5) and covers surface and drinking waters for the period from January through March 1976. (Ref. 12b)

2. Criteria for Radionuclide Concentrations in Water

In determining which radionuclides shall be measured to insure the public health and safety, both the prospects of their protracted ingestion by humans and the degree of regulation of permissible discharge must be taken into account. In the case of occupational exposure, the ICRP and NCRP have recommended maximum concentrations permissible in water (MPCw) on the basis of their studies of the dosimetry and metabolism of these nuclides. Calculations of MPC_w in occupational exposures must take into account the proviso that the long term ingestion of nuclides from water must not exceed the maximum burden allowed for any given organ. Thus, where more than one radionuclide is involved, each is treated as a fractional MPC_w value and the maximum permissible intake obtained from a consideration of the summation of these fractional exposures.

Guidance for determining suitable drinking water standards with respect to radionuclide concentrations for the general population is provided by ICRP, NCRP as well as the EPA. In the neighborhood of controlled areas and nuclear power plants recommended MPCw values for the general public are one tenth those specified for the occupational exposure (168 hr.) averaged over the entire year (Ref. 11 and 13).

Since 1970 development of U.S. Government policy with respect to human radiation exposure as applied to the general population has been the domain of the EPA. Prior to that date the FRC had developed guides involving levels of response designed to cope with the average intake of particular radionuclides (Ref. 13).

The Safe Drinking Water Act, Public Law 93-523, was passed December 16, 1974. Under the provisions of this act the EPA was required to publish National Interim Drinking Water Standards within 90 days:

NATIONAL DRINKING WATER REGULATIONS

"Sec. 1412. (a) (1) The Administrator shall publish proposed national interim primary drinking water regulations within 90 days after the date of enactment of this title. Within 180 days after such date of enactment, he shall promulgate such regulations with such modifications as he deems appropriate. Regulations under this paragraph may be amended from time to time."

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[a] See Table 5 of this text.

Interim primary drinking water regulations for proposed maximum contaminant levels for radioactivity were announced by the EPA on August 14, 1975 (Ref. 15). Table 6 lists some EPA interim primary drinking water standards (Ref. 15), permissible concentrations (AEC,‡ Ref.14) and daily intake guides (FRC, Ref. 13) for some radionuclides. Table 7 is a more detailed listing of maximum permissible concentrations of radionuclides for both air and water (Ref. 14).[a]

In 1974 the Environmental Protection Agency announced plans to issue new, stricter standards for environmental radiation from the nuclear power industry (Ref. 16) to apply only to planned releases and normal operations. These standards will be based on the conclusion of a prior NAS study that standards should be lowered and more consideration given to questions of total population dose and the cumulative effects of long-lived radionuclides (Ref. 17). The standards will not take into account the exigencies of a major reactor accident.

2.1 Radioactivity Criteria: Fresh Water

Criteria for drinking water in general apply to finished drinking water, since the commonly used water treatment processes (e.g., filtration, settling, softening, etc.) may reduce the activity of the raw water appreciably. It should further be noted that potential non-drinking water exposure pathways such as occur via radionuclide concentration in fish, vegetables, and live-stock in the food chain may often be of more concern than the drinking water itself.* For communities in which the treatment is minimal and where essentially raw water is consumed directly, the EPA has stated that the radioactivity should be as low as practicable at the public water supply intake, in no case exceeding the levels established in the Interim Drinking Water Regulations (DWR) (Ref. 15). Quoting:

TABLE 6. Radionuclide intake guides and permissible concentrations of some radionuclides in water.[a]

Radionuclide	Daily Intake, FRC, top of Range II, μCi (Ref. 13)	Permissible Concentration[b] ABC, μCi/ml (Ref. 14)	Drinking Water Standards, EPA pCi/ml (Ref. 15)
Unidentified	--	1×10^{-7c}	$5 \times 10^{-2\,d}$
^{3}H	--	3×10^{-4}	20
^{54}Mn	--	1×10^{-4}	--
^{58}Co	--	1×10^{-4}	--
^{60}Co	--	5×10^{-5}	--
^{89}Sr	2×10^{-3}	3×10^{-6}	--
^{90}Sr	2×10^{-4}	1×10^{-7}	1×10^{-2}
^{131}I	1×10^{-4}	3×10^{-7}	--
^{134}Cs	--	9×10^{-6}	--
^{137}Cs	--	2×10^{-5}	--
^{140}Ba	--	3×10^{-5}	--
^{226}Ra	2×10^{-5}	3×10^{-8}	3×10^{-3}

Adapted from Ref. 24.

[a] Data in columns 2, 3, and 4 are from Refs. 13,14 and 15.

[b] Concentrations of soluble radionuclides above natural background in effluents to unrestricted area.

[c] If ^{129}I, ^{226}Ra, and ^{228}Ra are not present, i.e., the concentration of each radionuclide is less than 0.1% of its permissible concentration.

[d] Gross beta activity in the absence of alpha emitters and ^{90}Sr.

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[a] For a complete listing of maximum permissible concentrations for radionuclides in both air and water, see Table 19 of the CRC Handbook (Ref. 6), pp. 617-631, inclusive.

* J.K. Channell, private communication (3/2/76)

‡ Superseded by ERDA (Energy Research and Development Administration)

TABLE 7. Maximum Permissible Concentrations of Radionuclides in Air and Water (Ref. 14).

Element	Atomic Number	Isotope*	A		B	
			In Air, μCi/ml	In Water, μCi/ml	In Air, μCi/ml	In Water, μCi/ml
If it is known that ^{90}Sr, ^{125}I, ^{126}I, ^{129}I, ^{131}I, (^{133}I, Section B only), ^{210}Pb, ^{210}Po, ^{211}At, ^{223}Ra, ^{224}Ra, ^{226}Ra, ^{227}Ac, ^{228}Ra, ^{230}Th, ^{231}Pa, ^{232}Th, ^{natural}Th, ^{248}Cm, ^{254}Cf, and ^{256}Fm are not present			—	9×10^{-5}	—	3×10^{-6}
If it is known that ^{90}Sr, ^{125}I, ^{126}I, ^{129}I, (^{131}I, ^{133}I, Section B only), ^{210}Pb, ^{210}Po, ^{223}Ra, ^{226}Ra, ^{228}Ra, ^{231}Pa, ^{natural}Th, ^{248}Cm, ^{254}Cf, and ^{256}Fm are not present			—	6×10^{-5}	—	2×10^{-6}
If it is known that ^{90}Sr, ^{129}I, (^{125}I, ^{126}I, ^{131}I, Section B only), ^{210}Pb, ^{226}Ra, ^{228}Ra, ^{248}Cm, and ^{254}Cf are not present			—	2×10^{-5}	—	6×10^{-7}
If it is known that (^{129}I, Section B only), ^{226}Ra, and ^{228}Ra are not present			—	3×10^{-6}	—	1×10^{-7}
If it is known that alpha emitters and ^{90}Sr, ^{129}I, ^{210}Pb, ^{227}Ac, ^{228}Ra, ^{230}Pa, ^{241}Pu, and ^{249}Bk are not present			3×10^{-9}	—	1×10^{-10}	—
If it is known that alpha emitters and ^{210}Pb, ^{227}Ac, ^{228}Ra, and ^{241}Pu are not present			3×10^{-10}	—	1×10^{-11}	—
If it is known that alpha emitters and ^{227}Ac are not present			3×10^{-11}	—	1×10^{-12}	—
If it is known that ^{227}Ac, ^{230}Th, ^{231}Pa, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{242}Pu, ^{244}Pu, ^{248}Cm, ^{249}Cf, and ^{251}Cf are not present			3×10^{-12}	—	1×10^{-13}	—

NOTE: In any case where there is a mixture in air or water of more than one radionuclide, the limiting values for purposes of this table should be derived as follows:

1. If the identity and concentration of each radionuclide in the mixture are known, the limiting values should be derived as follows: determine for each radionuclide in the mixture the ratio between the quantity present in the mixture and the limit otherwise established in this table for the specific radionuclide when not in a mixture. The sum of such ratios for all the radionuclides in the mixture may not exceed 1 (i.e., unity).

Example: If radionuclides A, B, and C are present in concentrations C_A, C_B, and C_C, and if the applicable MPC's are MPC_A, MPC_B, and MPC_C respectively, then the concentrations shall be limited so that the following relationship exists:

$$\frac{C_A}{MPC_A} + \frac{C_B}{MPC_B} + \frac{C_C}{MPC_C} \leq 1$$

2. ‡ If either the identity or the concentration of any radionuclide in the mixture is not known, the limiting values for purposes of this table shall be:
   a) for purposes of Section A, Column 1—6×10^{-13};
   b) for purposes of Section A, Column 2—4×10^{-7};
   c) for purposes of Section B, Column 1—2×10^{-14};
   d) for purposes of Section B, Column 2—3×10^{-8}.

3. (26 FR 11046) If any of the conditions specified below are met, the corresponding values specified below may be used in lieu of those specified in paragraph 2 above:
   a) if the identity of each radionuclide in the mixture is known, but the concentration of one or more of the radionuclides in the mixture is not known, the concentration limit for the mixture is the limit specified in this table for the radionuclide in the mixture having the lowest concentration limit; or
   b) if the identity of each radionuclide in the mixture is not known, but it is known that certain radionuclides specified in this table are not present in the mixture, the concentration limit for the mixture is the lowest concentration limit specified in this table for any radionuclide that is not known to be absent from the mixture; or
   c) (30 FR 15801).

4. (25 FR 13952) If the mixture of radionuclides consists of uranium and its daughter products in ore dust prior to chemical processing of the uranium ore, the values specified below may be used in lieu of those determined in accordance with paragraph 1 above or those specified in paragraphs 2 and 3 above:
   a) for purposes of Section A, Column 1—1×10^{-10} μCi/ml gross alpha activity; or 2.5×10^{-11} μCi/ml natural uranium; or 75 μg/m^3 air natural uranium;
   b) for purposes of Section B, Column 1—3×10^{-12} μCi/ml gross alpha activity; or 8×10^{-13} μCi/ml natural uranium; or 3 μg/m^3 air natural uranium.

5. (26 FR 11046) For purposes of this note, a radionuclide may be considered as not present in a mixture if a) the ratio of the concentration of that radionuclide in the mixture (C_A) to the concentration limit for that radionuclide specified in Section B of this table (MPC_A) does not exceed 1/10 (i.e., $C_A/MPC_A \leq 1/10$), and b) the sum of such ratios for all the radionuclides considered as not present in the mixture does not exceed 1/4 (i.e., $C_A/MPC_A + C_B/MPC_B + \cdots \leq 1/4$).

"The Environmental Protection Agency has adopted a policy which assumes that any dose of ionizing radiation has a potential to produce deleterious effects on human health...

Therefore:

"Estimates of possible health effects from maximum contaminant levels of radioactivity in drinking water have been based on the assumption that there is no harmless dose from ionizing radiation and that the detrimental effects on health produced will be proportional to the dose equivalent delivered to a reference man drinking two liters of water per day."

The rationale for proposed maximum contaminant levels for Ra-226 and other α-particle emitters is the high density energy transfer from emitted α-particles to the surrounding tissue. Ra-226 and Ra-228 pose additional hazards in that these isotopes produce a chain of α-emitting decay products which are retained in the bone. Consequently permissible dose from Ra varies with tissues at risk, the most important being the so-called trabecular bone surfaces. Bone dose is defined as the "dose received by endosteal ostegenic (i.e., bone-forming) cells in trabecular bone" since these are the critical cells for neoplastic[a] induction (Ref. 18). For bone-seeking radionuclides the organ dose is computed on the basis of dose at the bone surfaces; and the specified limiting concentrations for these isotopes are such that bone surface doses will be 0.06 rem/yr. maximum.

Radium-226 and Ra-228 doses for the bone marrow, gonads and other soft tissue sites which receive somewhat less exposures from metabolized radium have also been tabulated (Ref. 19). For a 10 pCi/day continuous ingestion of either isotope (e.g., 5 pCi/ℓ, 2 liters/day) the dose is 0.06 rem/yr to bone surfaces, 0.01 rem/yr to bone marrow, and 0.0002 rem/yr to soft tissues. By appropriate weighting of these dose rates at the various tissue sites it has been calculated that the continuous consumption of drinking water containing 5 pCi/ℓ α-activity in the form of Ra-226 or Ra-228 may be expected to result in 0.7 to 3 fatal cancers per million exposed population per year, with approximately two thirds of these being bone cancers (Ref. 20).

Current drinking water regulations for α-radiation are summarized below:[b]

a) for Ra-226, Ra-228 and other α-emitters; maximum Ra-226 and/or Ra-228 in raw water: 5pCi/ℓ

maximum gross α-particle activity (including Ra-226, but not U or Rn): 15pCi/ℓ

b) for large population concentrations, means should be examined to minimize population exposure, insuring the "as low as practicable" dose in man-rems or organ-rems.

Drinking water criteria for β-particle and photon-emitting activity from artifical radionuclides are set so as to limit any individual dose by ingestion to 4 mrem/yr. (Table 8) or about 0.25% of the maximum allowable industrial exposure. Whole body exposures for radiation workers are limited to 5 rem/yr by the FRC guide, or 330 times the former approved drinking water standard (PHS, 1962; Ref. 22).

The following excerpt from Ref. 15 reflects the reasoning behind the 4 millirem standard:[a]

> "Considering the sum of the deposited fallout radioactivity and additional amounts due to effluents from other sources currently in existence, the total dose equivalent from man-made radioactivity is not likely to result in a total body or organ dose to any individual that exceeds 4 millirem per year. Since present ambient-levels of man-made radioactivity are small, EPA does not believe that this standard will result in a need to remove man-made radioactivity from public water systems, nor subject the public to excessive risk.
>
> "For man-made photon and beta particle radiation to the total body, the potential risk of fatal cancer from a dose equivalent rate of 4 mrem per year, is about 0.4 to 2 cases per million exposed persons per year with risks from lower dose rates proportionally smaller. Additional health risks of genetic effects and non-fatal cancers are each estimated to be comparable to that for cancer fatality. Partial body irradiation is common for ingested radionuclides since they may, like radium, be largely concentrated in a particular organ system. In such cases, the estimated risk per rem varies depending on the radiosensitivity of the organs at risk. For example, the estimated number of thyroid cancers due to the thyroid gland receiving 4 mrem per year continuously range from about 0.2

TABLE 8. Limiting Annual Average Concentrations Assumed to Produce a Total Body or Organ Dose of 4 mrem/yr. (Ref. 15)

Radionuclide	Critical organ	pCi per liter
Tritium	Total body	20,000
Strontium-90	Bone marrow	8

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[a] Neoplasm: new cellular growth; this new growth is potentially malignant.

[b] These were promulgated in final form July 9, 1976 (Ref. 21).

[a] Analytically relevant sections are underlined for emphasis here and in all other excerpts of 40 CFR pt. 141 et. seq.

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to 0.5 per year per million exposed persons (averaged over all age groups). The fatality rate of thyroid cancers varies with age, from nearly zero for children and young adults to about 20 percent for persons well past middle age.

"The 4 millirem per year standard for man-made radioactivity was chosen on the basis of avoiding undesirable future contamination of public water supplies as a result of controllable human activities. Given current levels of fallout radioactivity in public water supply systems and their expected future decline, and the degree of control on effluents from the nuclear industry that will be exercised by regulatory authorities, it is not anticipated that the maximum contaminant levels for man-made radioactivity will be exceeded except in extraordinary circumstances."

Data published in the NAS-NRC report (Ref. 17) have been used to estimate both total body and partial body exposures. These estimates are based on the "conservative" assumption that the number of cancers/rem of radiation observed at high doses and dose rates may be used to predict radiation effects at the lower doses and dose rates encountered environmentally. The actual degree of conservatism in this assumption remains to be documented. It is, however, likely to be less for ingested α-emitters than for artificial radionuclides decaying by β- or γ-ray emission.

The individual risk estimated for a fatal cancer calculated using alternate NAS-BEIR[a] models for the 1967 U. S. population ranges from 0.4 to 2×10^{-6} per year for a total body dose of 4 millirem/yr to an exposed group with the same age distribution, the value obtained depending on which model was used -- *absolute* or *relative*.[b]

Rather than choosing between the two models the committee uses an average value for their "most likely estimates". This leads to a value about twice as great as the absolute risk. By comparison, it is estimated that the individual risk of fatal cancer from all causes is more than 500 times as great (Ref. 17).

Detrimental effects of a genetic nature are more difficult to estimate. Their total increase over a span of several generations would, however, be comparable to the increased incidence of cancer, according to the NAS-72 report.

In the more common case of partial body irradiation, as with the medical ingestion of radionuclides, the estimated risk of cancer is lower. Thus, continuous exposure of the thyroid gland to 4 mrem/yr yields cancer risk values from 0.2 to 0.5 10^{-6}. Fatality from thyroid cancer is age-dependent, ranging from nearly zero for children and young adults to approximately 20% for individuals well beyond middle age. Although thyroid exposure appears to have a less deleterious effect than that of whole body exposure, it should be noted that the Drinking Water Regulations do not reflect these differences. Neglect of this factor is justifiable, however, since the "error", or the degree of public health protection introduced thereby, is of the same order of magnitude as the uncertainties introduced in calculation of the risk estimates themselves. Also, the greater sensitivity of young children to thyroid exposure, now well-documented (NAS/NRC-72), strongly suggests the need for extreme caution in establishing these standards.

Proposed Interim Primary Drinking Water Standards were circulated for comment in a preliminary draft form by the EPA on January 23, 1975 (Ref. 23), and a later revision published in the Federal Register (Aug. 14, 1975; Ref. 15). Regulations for radioactivity were promulgated in their final form on July 9, 1976 (Ref. 2[illegible]; App. 2). Table 9 (Ref. 15) examines the impact of reduction in the allowable limits for radium on three parameters: 1) the number of water supplies affected, 2) annual cost, and 3) the estimated number of cancer fatalities averted per year.

The maximum contaminant level of 5 pCi

TABLE 9. Comparison of Radium Control Limits (Ref. 15)

Control limit pCi per liter	Estimated number of supplies impacted	Annual cost to achieve limit	Estimated total number of lives saved per year
9---------	240	$ 1,400,000	0.6
8---------	300	2,400,000	1.1
7---------	370	3,400,000	1.6
6---------	450	5,600,000	2.5
5---------	500	8,800,000	3.7
4---------	670	14,000,000	5.5
3---------	800	24,000,000	8.2
2---------	860	36,000,000	11
1---------	980	70,000,000	15
0.5-------	1,100	100,000,000	20

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[a] Biological Effects of Ionizing Radiation.

[b] *Relative risk*: based on calculated percent increase of the "spontaneous" cancer mortality rate/rem. *Absolute risk:* approximately one fourth the relative risk (for a lifetime cancer risk), based on the observed number of cancer deaths/rem in an exposed population (e.g., Hiroshima, Nagasaki).

per liter finally proposed for radium gave due consideration to all three factors. For the man-made emitters, the proposed standards serve to limit future contamination of public water supplies as a result of controllable human activities (Ref. 15). For comparison, some typical radionuclide concentrations found in U. S. waters are given in Table 10.

Compliance with sections 141.16 of the DWR (Maximum contaminant levels of β-particles and photon radioactivity from man-made radionuclides) is defined as follows:

> (b) Compliance with this section may be assumed if there is a gross beta particle activity of less than 50 pCi/l and if the concentration of tritium and strontium-90 are less than those listed in Table A[a]: *Provided that*, if both radionuclides are present the sum of the annual dose equivalents to bone marrow shall not exceed 4 mrem. If the gross beta particle activity exceeds 50 pCi/l, a radiochemical analysis of the sample must be performed to identify the radioactive constitutents, and the appropriate total body and organ doses must be calculated. If two or more radionuclides are present, the sum of the annual dose equivalents to the total body or any organ shall not exceed 4 millirems.
>
> (c) Except for the radionuclides listed in Table A, the concentration of man-made radionuclides causing 4 millirem total body or organ dose equivalents shall be calculated on the basis of a 2 liter per day drinking water intake and using the 168 hours data listed in 'Maximum Permissible Body Burdens and

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[a] See Table 8 of this section.

TABLE 10. Typical Radionuclide Concentrations in Water (Ref.24)

Radionuclide	Concentration, pCi/liter[a]	Date
	U.S. surface waters	
Gross alpha	0-35	Dec. 1968
Gross beta	2-65	Dec. 1968
^{3}H	800[b]	Jan.-June 1968
^{90}Sr	2	April-June 1967
^{210}Pb	0.04	–
^{222}Rn	1-100	–
^{226}Ra	0.14	–
^{238}U	<1	–
	Ocean water	
^{3}H (natural)	0.6-3	–
^{14}C	0.1	–
^{40}K	300	–
^{87}Rb	2	–
^{90}Sr	0.14	Jan.-June 1965
^{238}U + progeny	3	–
All other (natural)	<0.2	–

[a] 1 pCi/liter = 1×10^{-9} μCi/ml.

[b] The average does not include concentrations in water downstream from AEC installations on the Columbia, Savannah, and Clinch Rivers, for which average concentrations were 6000 pCi/liter. Adapted from Ref.24, p.1364.

Maximum Permissible Concentration of Radionuclides in Air or Water for Occupational Exposure", NBS Handbook 69 as amended August 1963, U. S. Department of Commerce.[a]

A more recent revision of the DWR appeared too late for incorporation into this section (see Appendix 2). Currently the EPA is circulating internally a revised draft of a Water Criteria Document for which no publication date is available.[b] All that can be stated with reasonable assurance is that the final criteria established must be compatible with the DWR promulgated.

2.2 Radioactivity Criteria: Saline Waters

An acceptable level of any given radionuclide in sea water depends on its potential for concentration in edible marine organisms harvested for human consumption. The annual dose to "the most exposed group" using the food must not exceed the individual yearly dose prescribed for drinking water (1974 criteria, V. C.; Ref. 25).

Prior to 1944 all radiation in marine waters came from natural sources with potassium-40 the major source (90%) of radiation. However, during the past thirty years, additional sources of radionuclide contamination were provided, first by nuclear weapons testing and later by nuclear-powered ships and submarines as well as by nuclear power and fuel reprocessing plants. Quantitative measurement of amounts of radiation affecting marine life is difficult because of the multiple exposure paths operant: 1) food chain, 2) surface radioisotope adsorption from the aquatic environment, and 3) from radioactive sediments. However, it is known that isotopic concentration in aquatic organisms can indeed be large: factors range as high as 50,000 in phytoplankton, 25,000 in zooplankton, 5,000 for benthic algae, 2,500 for crustacean muscle tissue, and 1,600 for fish muscle. Zinc and manganese may be concentrated in the edible portion of shellfish by factors of 11,000 and 12,000 respectively (Ref. 26). Table 11 lists concentration factors for the more common aquatic organisms. For a more detailed listing of suggested concentration factors for radionuclides derived from groups I through VIII

TABLE 11. Concentration Factors for Aquatic and Marine Organisms (Ref. 26)

Radionuclide	*Organism*	*Concentration Factor*	*Reference*
Sodium-24	**Marine invertebrates**	0.5	3375
	Fresh-water fish	100	2436
Phosphorus-32	***Spirogyra***	850,000	3273
	Caddis-fly larvae	370,000	2535
	Insect larvae	200,000	3304
	Shiners	165,000	2535
	Fish	30,000–100,000	2436
	Marine vertebrates	40,000	3375
	Algae (*Ochromonas*)	4,900–10,500	3386
	Algae (*Platymonas*)	6,300–13,600	3386
Sulfur-35	**Marine invertebrates**	5	3375
Potassium-42	**Marine algae**	25	2440
	Marine invertebrates	10	2440, 3375
	Marine vertebrates	5	2440
	Crabs (*Carcinus*)	4	3820
Calcium-45	**Marine invertebrate, skeletons**	1,000	2440
	Marine invertebrate, soft parts	10	2440, 3375
	Marine vertebrate, skeletons	200	2440
	Marine vertebrate, soft parts	1	2440
	Marine algae	10	2440
Iron-59	**Algae (6 species)**	720–7,500	3386
	Fresh-water fish	10,000	2436
	Marine algae	20,000	2440
	Marine invertebrates, skeletons	100,000	2440
	Marine invertebrates, soft parts	10,000	2440, 3375
	Marine vertebrates, skeletons	5,000	2440
	Marine vertebrates, soft parts	1,000	2440
Chromium-51	**Brown Algae**	100–500	2442
Cobalt 60	**Algae (*Ochromonas*)**	1,070–1,500	3386
	Diatom (*Navicula*)	271	3386
	Copepoda	50	2444
	Marine plankton (maximum)	10,000	3375

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[a] Ref. 11.

[b] Private Communication from James K. Channell, Chief, Hazardous Materials Branch, EPA Region IX.

TABLE 11. Concentration Factors for Aquatic and Marine Organisms. (Continued)

Radionuclide	*Organism*	*Concentration Factor*	*Reference*
Copper-64	**Algae (*Ochromonas*)**	1,840-3,040	3386
	Sphaerotilus	3,300	3386
	Marine bacteria	900	3386
	Marine invertebrates, soft parts	5,000	3375
	Fresh-water fish	50	2436
Zinc-65	**Algae (6 species)**	312-67,800	3386
	Brown algae	400-1,400	2442
	Marine bacteria	200	3386
	Marine invertebrates, soft parts	5,000	3375
	Oysters	200,000	2446
	Oyster meat	1,400	2442
Strontium-89 & 90	**Algae (6 species)**	100-3,000	3386
	Brown algae	8-90	2442
	Algae	1,840-2,110	3385
	Diatom (*Nitzschia*)	17	3600
	Algae	1-40	3819
	Crustacea	3-6	3819
	Mussels (*Mytilus*)	6	3819
	Brine shrimp	40	3821
	Bacteria	10-100	3822
	Marine bacteria	100	3386
	Marine algae	20	2440
	Marine invertebrates, skeleton	1000	2440
	Marine invertebrates, soft parts	10	2440, 3375
	Marine vertebrates, skeleton	200	2440
	Marine vertebrates, soft parts	1	2440
	Rudd, flesh	2.6	3601
	Rudd, bone	71	3601
	Rudd, scales	209	3601
	Fresh-water fish	20,000-30,000	2436
	Goldfish	10-150	3823
	Goldfish	35-53	3824
	Mosquito-fish, live	1.6-3.1	3385
	Mosquito-fish, dead	2.7-48.8	3385
Ruthenium-103 & 106	**Algae**	104,000	3385
	Algae (*Ochromonas*)	4,000-6,500	3386
	Diatom (*Navicula*)	7,900	3386
Iodine-131	**Copepods**	200	2444
	Marine algae	10,000	2440
	Marine invertebrates, skeleton	50	2440
	Marine invertebrates, soft parts	100	2440, 3375
	Marine vertebrates, soft parts	10	2440
Cesium-134 & 137	**Algae (6 species)**	20-2,180	3386
	Green algae	400-4,000	3387
	Fresh-water algae	52-1,530	3388
	Algae	342,000	3385
	Green, red & brown algae	4-30	3819
	Crustacea	10	3819
	Marine algae	1	2440
	Marine invertebrates, soft parts	10	2440
	Marine vertebrates, soft parts	10	2440
	Oysters, soft tissue	60	3375
	Crabs (*Carcinus*)	8	3820
	Mussel (*Mytilus*), soft body	10	3819
	Flavobacterium aquatile	26	3386
	Sphaerotilus	116	3386
	Marine bacteria	15	3386
	Zooglea ramigera	558	3386
	Snail	600	3387
	Amphipods	11,000	3387
	Tadpoles	2,600-6,000	3387
	Damsel-fly & dragon-fly nymphs	800	3387
	Bullfrog, muscle	9,000	3387
	Carp, muscle	3,000	3387
	Sunfish, muscle	8,500	3387
	Atlantic prawn	25	2444
Cerium-141 & 144	**Algae (4 species)**	5,100-28,300	3386
	Algae (several species)	2,000-4,500	3272
	Algae	2,040,000	3385
	Algae	314-4,498	2442
	Red, green & brown algae	300-900	3819
	Mussel (*Mytilus*), soft body	300	3819
	Crustacea	230	3819
	Marine bacteria	290-1740	3386
Gross beta emitters	**Algae**	43,300	3385
	Plankton	4,210	3825
	Bottom animals	526	3387
	Shiners, juvenile	474	3825
	Suckers, bone	263	3825
	Suckers, muscle	58	3825
	Bass, bone	184	3825
	Bass, muscle	24	3825
Mixed fission products	**Algae (6 species)**	1,700-16,300	3386

inclusive, Freke's article should be consulted (Ref. 27). The NRC currently uses these data in its calculations.

Adsorbed and absorbed radioactivity may affect marine organisms in a variety of ways, causing damage at both cellular and molecular levels. The effects may range all the way from developmental and physiological changes and abnormalities to growth inhibition, behavioral changes, reduction of life span, or death. The effects may be enhanced *(synergism)* by the contributions of other environmental stresses (e.g. changes in salinity, temperature, etc.). Such changes may be of the gross pathological sort which can be readily observed or of a more subtle nature, not readily detectable. Changes may be *somatic*, affecting the individual organism or *genetic*, resulting in deleterious effects on later generations of offspring.

Sensitivity to radiation varies with the complexity of the test organism: algae and bacteria may tolerate thousands of rads; fish a thousand rads. But fish eggs and early developmental stages are more sensitive to radiation by an order of magnitude or more than the adult forms of the species.

D. ANALYTICAL CONSIDERATIONS

Since the number of radionuclides which could conceivably be present in a sample is large, some initial delimitation is desirable. This step should supply information on the need for chemical separation and for detectors to eliminate interferences; it should also ascertain the utility of gross activity measurements in the sample. Once the sample source has been identified, further consideration of such factors as a) specific radionuclides generally associated with the source, b) their chemical properties and c) their half-lives can be used to determine the analyses necessary.

In the absence of specific source information, more generalized factors such as isotope abundances, half-lives, and production cross sections may prove useful. Radionuclide charts (Ref. 28) may be consulted, as well as tables of isotopes (Ref. 29, 30).

Radionuclides with half-lives too short to measure, and those with very long half-lives, (i.e., very low specific activities), need not be measured. Table 12 lists some of the artificial and naturally-occurring radionuclides which may be found in water. For the natural nuclides, concentrations in water are a function of their solubilities, whether they derive from air in contact with the water (i.e., H-3, Be-7, C-14), or from minerals containing K-40, Th or U. In addition, the longer-lived radionuclides contributed by fallout are now present in those waters that were exposed to air or to contaminated surfaces during fallout periods. Included among these nuclides are the following: a) activation products: H-3, Mn-54 and Fe-55; b) fission products: Sr-90, Ru-106, Sb-125 Cs-137, Ce-144, Pm-147.

TABLE 12. Radionuclides Commonly Produced by Fission and Activation and Occurring in Nature[a],[b],[†]

Fission products – thermal neutron ^{235}U fission yield > 0.1%, 0.8 d < $t^c_{1/2}$ < 1 × 10^7 d		
10.7-yr ^{85}Kr	93.-hr ^{127}Sb	32.4-d ^{141}Ce
50.5-d ^{89}Sr	34.-d ^{129m}Te	33.-hr ^{143}Ce
28.5-yr ^{90}Sr	30.-hr ^{131m}Te	13.6-d ^{143}Pr
64.0-hr ^{90}Y	8.06-d ^{131}I	284.-d ^{144}Ce
59.-d ^{91}Y	78.-hr ^{132}Te	11.1-d ^{147}Nd
65.-d ^{95}Zr	20.9-hr ^{133}I	2.62-yr ^{147}Pm
35.1-d ^{95}Nb	2.3-d ^{133m}Xe	53.-hr ^{149}Pm
66.2-hr ^{99}Mo	5.29-d ^{133}Xe	28.-hr ^{151}Pm
39.6-d ^{103}Ru	30.-yr ^{137}Cs	90.-yr ^{151}Sm
36.0-hr ^{105}Rh	12.8-d ^{140}Ba	47.-hr ^{153}Sm
369-d ^{106}Ru	40.3-hr ^{140}La	
Activation products accompanying fission, 0.8-d < $t^c_{1/2}$ < 1 × 10^7-d		
2.07-yr ^{134}Cs	2.34-d ^{239}Np	24,400-yr ^{239}Pu
13.-d ^{136}Cs	88.-yr ^{238}Pu	163.-d ^{242}Cm
Activation products in nuclear reactor material, 0.5-d < $t^c_{1/2}$ < 1 × 10^7-d		
12.3-yr ^{3}H	270.-d ^{57}Co	55.-hr ^{115}Cd
5730.-yr ^{14}C	71.3-d ^{58}Co	2.7-d ^{122}Sb
15.0-hr ^{24}Na	44.6-d ^{59}Fe	60.2-d ^{124}Sb
14.3-d ^{32}P	5.26-yr ^{60}Co	42.5-d ^{181}Hf
[illegible].0-d ^{35}S	92.-yr ^{63}Ni	115.-d ^{182}Ta
27.7-d ^{51}Cr	12.8-hr ^{64}Cu	5.0-d ^{183}Ta
313.-d ^{54}Mn	244.-d ^{65}Zn	75.-d ^{185}W
2.7-yr ^{55}Fe	253.-d ^{110m}Ag	24.-hr ^{187}W
Naturally occurring long-lived radionuclides		
12.3-yr ^{3}H	1.40 × 10^{10}-yr ^{232}Th and progeny	
53.-d ^{7}Be	7.13 × 10^{8}-yr ^{235}U and progeny	
5730.-yr ^{14}C	4.51 × 10^{9}-yr ^{238}U and progeny, including 1600-yr ^{226}Ra	
1.28 × 10^{9}-yr ^{40}K		

[a] *Half-lives and fission yields are given in Refs. 29, 30, 68, 69.*

[b] *Abbreviations: hr = hour, d = day, yr = year.*

[c] *Range of $t_{1/2}$ and fission yield used in the search for listed isotopes.*

[†] *Adapted from table 3 ref. 24, p. 1363.*

There has been extensive study of radionuclide transport in environmental aquatic systems in connection with efforts to predict their concentrations in the aquatic food chain and in drinking water (Ref. 24). These predictions must also take into account the chemical characteristics of the nuclide in question since these properties will affect concentration in the aqua system. The factors of solubility as well as other natural removal processes will affect the radionuclide content of a sample. Table 10 lists typical concentrations of natural radionuclides as well as those occurring in fallout, as they appear in surface and ocean waters in the United States. There may be considerable variation in the concentrations found, depending on the sample source. Thus rain-water and certain nuclide-concentrating biota, yield higher concentrations of radionuclides from fallout. An expanded list of nuclides from all sources is given in Table 12.

For monthly reports of radionuclide concentrations in water and other media see Ref. 31. The United Nations Scientific Committee on the Effects of Atomic Radiation publishes a biennial review (Ref. 32) which includes radionuclide concentration information.

Shorter lived high-yield radionuclide fission products are generally present in rainwaters shortly after atmospheric nuclear testing. Nuclides encountered under these circumstances include Sr-89, Nb-95, Zr-95, Ru-103, I-131, Ba-140, and Ce-141, and may be detected for periods equivalent to several half-lives.

Activity may also occur in effluents other than rainwater, such as surface- and groundwaters, and is dependent on a variety of factors, including pathway and point of release. The Nuclear Regulatory Commission (formerly Directorate of Regulation of the AEC), receives reports of discharge data from commercial nuclear power plants.

Radioactive tracers are used in a variety of fields ranging from agriculture to the study of water supplies; from forestry and hydrology to mining. All of these uses add radioactive pollutants to waters. Where suitable alternate methods are available, it is recommended that they be employed. When radio-nuclide tracers must be used, the amounts used should be minimized and the choice of nuclide made with a strong bias toward minimizing exposure of resident biota to radiation. Naturally the selection of an appropriate tracer to do a particular job will involve other considerations as well; namely, compatibility of the tracer characteristics with the requirements of the parameter measured, minimum interference from other substances, and ease of detection. Shortlived tracers should be given preference where possible, and the presence of a suitable indicator radionuclide in the system should be explored before "spiking" it with an extraneous tracer.

1. Sampling For Radionuclide Analysis

In general, the principles of good sampling techniques which are applicable to water analysis for other parameters apply here as well, and the reader is encouraged to review the discussion of sampling under H_2O-BIO:BOD. See also sections 105 A.3 and 701-A (Ref. 5), and 3370-T (Ref. 4). The following discussion will therefore deal only with those areas of sampling wherein radionuclide sampling and analysis present unique problems.

Because radionuclides may often exist in submicrogram quantities in fresh water samples, any loss by surface *adsorption* on containers could be significant in terms of the percent loss. Radionuclide adsorption by suspended particulates pose a similar problem.

In the sampling of radioactive industrial wastes with higher levels of activity, the possibility of container contamination exists. Adsorption of radioactivity on the walls of glass or plastic containers not only will result in a low sample analysis, but introduces the further risk of radioactive contamination of later samples by virtue of subsequent *desorption* of activity from container walls. Thus re-used containers must be scrupulously cleaned to remove adsorbed activity.

Sampling frequency and duration is dictated by the information required of the analysis and the need to collect a representative sample. Compositing of radioactive samples is generally similar to that required in sampling of waters for purposes of measurement of other parameters. Collection times and the relative quantities of each sample in a composite should be recorded when radioactive decay estimates are to be calculated.

1.1 Precautions

For most environmental samples the activity is sufficiently low that no special safety precautions are needed. However, special handling may sometimes be required, to avoid the exposures associated with radioactive process waters.[†] For detailed information on radiological hazards and recommendations on protection, the reader should consult references 4, 5, 6, 13, and 14.

In the sampling of waters where activity may be high, (e.g., nuclear reactor cooling waters) specific health physics regulations are applicable and must be observed. This may on occasion involve the wearing of suitable protective clothing and the use of personnel monitoring devices. For sampling areas with a sufficiently high level of activity to constitute a radiation hazard, shielding may be necessary for sampling lines and auxiliary equipment, such as collection devices, coolers, etc. Special precautions must be exercised to prevent radioactive contamination by leaking or spillage of samples, breaking of sample lines, containers, valves and other equipment. Release of gaseous or airborne activity must also be avoided to protect sampling personnel.

Specially packed and shielded containers are used to ship radioactive samples, in compliance with shipping regulations for these materials.

[†] See Ref. 4, Sampling Method 3370-74T, Section 14.3, Sampling Radioactive Water.

1.2 Apparatus

Specifications for sampling apparatus, including items such as valves, sample lines, containers and coolers, and shipping containers are detailed in the 1975 Book of ASTM Standards (D-1192, Ref. 4). The choice of an appropriate sample container depends on the sample activity and its physical state For radioactivity measurement, plastic containers are generally preferred.

1.3 Pretreatment

If the water sample contains suspended solids (SS), the distribution of activity between solution and suspension should be ascertained. Under these circumstances, it will be necessary to filter a known volume of the sample, which will vary with sample activity. Methods applicable to (SS) are described in D 1888 (Ref.4). Filtration is normally carried out at room temperature (RT) using suitable filtrants. The latter include cellulose ester membranes, paper and fritted glass filters for use at RT, and sintered metals such as Ni, stainless steel and Pt for use at elevated temperatures. Filtration should be done immediately after sample collection (or at the earliest practicable moment).

Since radioactive SS collected on a filter may present an airborne inhalation hazard, appropriate precautions must be taken in handling the precipitate.

The preparation and handling of sample containers is described in ASTM D-1192 (Ref. 4). Plastic or wax-coated containers minimize loss of activity through adsorption on container walls. Addition of acids or complexing agents may sometimes be used to accomplish this end. However addition of acids may affect the distribution of activity between dissolved and suspended phases. In the case of analysis for specific radionuclides, stable *carrier* isotopes are sometimes added to facilitate analysis and minimize the losses. When water containing radioactive gases is sampled under pressure, special precautions must be taken to avoid excessive losses of these gases. This may be accomplished by appropriate container design.

Short-lived activity requires very rapid sample analysis to minimize decay loss. Analysis of long-lived species may often be simplified by delaying the operation until the shorter-lived species have decayed.

2. Analysis for Radionuclides: General Procedures

Operationally, analytical procedures generally consist of two parts. The first is designed to effect chemical separation and concentration of the radionuclides and removal of interferences. The second involves detection of the isolated or separated radionuclide.

2.1 Separation

The water sample is chemically treated to convert to a suitable chemical form, isolate or concentrate the nuclide (precipitation, sequestering or complexing, oxidation, reduction, etc.) Such separations are employed in: a) the measurement of gross α- and/or β-activities in low activity samples of high salinity, and in b) the analysis of samples emitting little γ-radiation; c) investigation of sequential decay patterns in a genetically-related series, and d) as confirmatory checks on instrumental identifications of nuclides. By a judicious selection and combination of chemical and instrumental analytical methods, radionuclides may be identified and quantitated with a high degree of certainty and precision.

Radionuclides in water samples are generally at such low concentrations that the solubility constants are not exceeded. Thus they cannot be precipitated alone. At such low concentrations, a substance may exhibit atypical behavior quite different from what is characteristic of it at conventional *macro-* (or even *micro-*) concentrations. The reasons for these behavioral differences may lie in the influence of other trace substances in solution, ion exchange phenomena involving container surfaces, hydration, complexation by organics and a variety of ionic and/or molecular interferences of a second order nature which may not become evident in higher concentration analyses. These effects are lumped together under the general rubric of *radiocolloidal effects* (Ref. 33).

Because of the unique analytical problems presented by the submicromolar concentrations of radionuclides encountered, it is customary to employ *carriers* in radiochemical procedures. By the initial addition of either an isotopic or non-isotopic carrier to the sample, it is possible to overcome these radiocolloidal effects and to monitor percent recovery at the conclusion of a procedure simultaneously. Generally the carrier consists of a standard solution of reagent which mimics the chemical characteristics of the isotope and thus carries it along in the analysis. In routine analyses the carrier will be the same element and in the same oxidation state or chemical form as the radionuclide itself. However, where the desired isotopic carrier is not available, a carrier in the same chemical group as the nuclide is employed. Thus the radioisotopes of Tc, Pm and Ra have been carried with the stable forms of Rh, La and Ba, respectively. Carrier concentrations are adjusted so that the final weight of the sample prepared for counting is ≈ 20 mg.

In addition to obviating radiocolloidal effects and monitoring percent recovery, the use of carrier techniques makes quantitative recovery of the nuclide unnecessary by substituting the criterion of *chemical yield* (recovered carrier/added carrier). This quantity automatically corrects for any loss of radionuclide, thereby expediting and simplifying the analytical procedure.

Because of the low concentrations of radionuclides, it is frequently necessary to collect and concentrate large water samples. The concentration step may be effected by bulk evaporation, or by means of automatic injectors which periodically deliver small aliquots for evaporation into a heated chamber.

As mentioned previously, the concentration of radionuclides is also carried out by other techniques involving procedures such as co-precipitation, ion exchange, solvent extraction --all standard analytical techniques. Radionuclides may also be concentrated in distinct groups by precipitation of their basic carbonates or sulfides, or their insoluble hydroxides. The application of ion exchange techniques to water samples of low ionic strength may also be used to collect groups of isotopes (Refs. 3, 34, 35).

Identification of the elemental radionuclide often involves a complex purification procedure to remove impurities which may be present at concentrations which are greater by orders of magnitude than the radionuclide concentration. Each radionuclide and its carrier must be purified by a species-specific technique and may involve a number of separation steps designed to remove individual major interferences in parallel with the impurities. *Holdback reagents* are customarily used to render the behavior of active impurities more predictable as well as to facilitate their removal by precipitation (Ref. 24).

Where inactive species may interfere with either carrier yield determination or with radionuclide detection, they too, must be removed. Thus, solids may lower the α-particle count if present at a surface density of >5 mg/cm^2. This is also true for other weak radiations (β's and x-radiation). Although the reduced counting *rate* may be of itself acceptable, the presence of solids at these levels may affect the reproducibility of counting *efficiency* with sample weight. Worse yet, yield determinations are affected by amounts well below those of concern for counting efficiency alone. Thus, 2 mg of an inactive contaminant in 20 mg of carrier may result in a significant overestimation of the yield.

Carrier recovery determinations are best performed gravimetrically for the following reasons: a) both the activity and the yield measurements are done on the same sample in its entirety; b) the intact precipitate may be used for further measurements if needed.

The criteria with respect to reproducibility and stability, discussed previously, naturally apply for gravimetric measurements as well. Where a gravimetric method is too time-consuming or poses other disadvantages, other non-destructive procedures may be substituted (e.g., colorimetry) either prior to or after counting the sample, or in an aliquot of the counted sample. (Ref. 24).

Where a separated nuclide decays to another active species, separation of the daughter is not only a confirmatory step, but also may be used to distinguish between isotopes of the same element and to provide further purification. Thus, Sr-90 may be measured in the presence of Sr-89 by purification of the Sr followed by storage of the sample for a time equivalent to several half-lives of the 64-hr daughter Y-90. The Y-90 is then separated and counted (after the addition of carrier) and the yield determined. The product of the fractional parent recovery and the daughter recovery gives the overall yield of daughter.

Procedures for radiochemical separations may be adapted as needed from the radioanalytical methods already available in the literature.[†] Often these methods are adequate without further modification. Sometimes it is necessary to develop totally new separations based on fundamental separation chemistry. A newly developed procedure should be tested for the limits of sample composition for which it is valid as regards radionuclide-carrier exchange, yield of carrier, and sample purification (*decontamination;* Ref.24). Such information will be most reliable if provided by the radionuclides present in the sample itself. In the event that their concentrations are too low to make this practicable, radioactive tracers may be employed -- provided they are constituted in the same chemical form as the nuclides to be measured.

Analytical quality control procedures employed in radioanalytical chemistry are very similar to those employed by analytical chemists working with non-radioactive species. Namely, continuous control is maintained by means of knowns, replicates and blanks, preferably analyzed *blind* along with unknowns. Knowns are generally prepared in large batches, their activity measured either on aliquots, or on the latter spiked with a previously standardized radionuclide aliquot. The knowns verify radioactivity and yield measurements.

[†] References 4 and 5 give standard analytical procedures for gross α- and β-determinations as well as chemical methods for individual nuclides normally encountered in water samples. Where other specific or unusual problems are encountered, the analyst should consult Ref. 3, N.S.A., and the biennial summaries published by *Analytical Chemistry*. The nuclear chemistry section of *Chemical Abstracts* also provides broad coverage of the literature in this field.

Replicates provide an indication of analytical precision; and blanks, since they do not contain added unknowns, provide the count background for an analysis as well as a means of detecting radioactive contamination anywhere in the analytical chain, from apparatus and reagents to the final detection step.

2.2 Specific Procedures:

2.21 Total Strontium

The following procedure for total radioactive strontium (Sr^{89} and Sr^{90}) is abstracted from Standard Methods (14th ed). The reader may consult Section 704 for the more detailed procedure. It is applicable either to total strontium or Sr^{90} analysis in drinking water or in filtered raw water. If sewage and industrial wastes are treated to remove organic matter and interfering inorganics, the same method is applicable to samples from these sources as well:

1) A known amount of $Sr(NO_3)_2$ is added as the carrier.

2) Radiostrontium in the sample is concentrated by co-precipitation of the carbonate with the carrier strontium and other alkaline earths (plus the rare earths).

3) The desired radiostrontium and carrier are then separated from other radionuclides and inactive contaminants by repeated precipitations as the nitrate from fuming nitric acid.

4) The purified nitrates are redissolved and precipitated as carbonates, dried and weighed to determine carrier recovery.

5) Activity of the purified precipitate is from radiostrontium only. Loss of carrier and activity is compensated by a correction in the final calculation for Sr. By delaying the count one obtains an increased counting rate due to the ingrowth of yttrium-90.

6) Total strontium activity is calculated from Eq. (13) as follows:

$$\text{Total Sr activity (pCi/}\ell) = \frac{h}{adf \times 2.22} \qquad (13)$$

a = beta counter efficiency

$$d = \frac{\text{mg final } SrCO_3}{\text{mg } SrCO_3 \text{ in 2 ml of Carrier}}$$

= corr. for carrier recovery

f = sample volume (liters)

h = beta activity in net counts/min = $(i/t) - k$

i = total accumulated counts

t = time of counting in minutes

k = background, counts/min.

2.22. Radium: Analytical Methods

Standard Methods (Ref. 5, pp.674-7) describes separate procedures for determining dissolved and undissolved radium in water, using a membrane filter to separate the suspended matter for dissolution with Nicholson's flux. The reader should consult Ref. 5 for details of these procedures. Here, however, we will discuss a number of the techniques which employ chemical separation of radium followed by counting or spectroscopy of the radium alphas.

2.221 Radiochemistry with Radium Alpha Counting

Ordinary chemical techniques are intrinsically incapable of differentiating among the various radium isotopes. Thus if simple alpha counting is used, a single measurement can only yield total radium activity. Alpha spectroscopy, on the other hand, enables the various alpha energies to be separately identified quantitatively. Another technique for separating isotopes is to make activity measurements at several different times, so that the build-up and decay of activities from the various radium/daughter series can be followed. The basis for this can be seen in Fig.5, which shows the theoretical growth and decay of total alpha activity (parent plus daughters) into pure radium isotopes. This

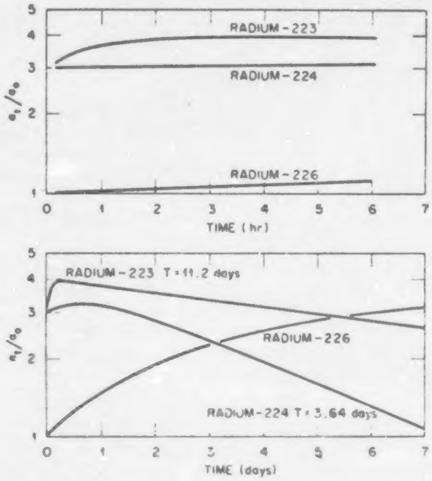

FIGURE 5. Growth of alpha activity into pure radium isotopes (Ref. 1c).

time variation can be used to determine ratios of ^{226}Ra: ^{224}Ra: ^{223}Ra.

The section "Alpha Particle Instrumentation" in Volume 3 of this series contains detailed discussions of instruments for alpha counting and spectroscopy. In summary, internal gas proportional counters, solid state (surface-barrier) detectors, pulse ion chambers, and scintillators are among the more common alpha instruments in use.

Because the range of alphas in matter is so small (~5 to 10 mg/cm^2), one problem for the chemist is preparation of a sample thin enough to be counted without important self-absorption corrections. For alpha spectroscopy this is particularly difficult.

Some techniques for radiochemical determination of specific radium isotopes by measuring their daughters (lead, polonium, bismuth) will be discussed below.

Standard Methods (13th Ed.) describes a technique designed for the screening of drinking water. The method is also applicable to sewage or industrial wastes provided that organic matter is destroyed:

Lead (nitrate) and barium (chloride) carriers are added to the sample containing alkaline citrate. Sulfuric acid is added to precipitate radium, barium and lead as the sulfates. The precipitate is then purified by washing with nitric acid, dissolved in alkaline EDTA, and re-precipitated as radium-barium sulfate after adjusting the pH to 4.5. This slightly acidic EDTA keeps other naturally occurring alpha emitters, and the lead carrier, in solution. The precipitate is counted with an internal gas proportional counter, after a 3 to 18 hour wait. To determine isotopic mixtures, additional counting at 7, 14 or 28 days may be carried out, depending on the number of isotopes in the mixture. Amounts of the various isotopes present can be determined by solving a set of simultaneous equations.

Average chemical recoveries are excellent (~ 97%) in this method, and the technique is valuable as a screening method for routine radium-in-water analysis. Details of the method may also be found in Ref. 5, pages 663-5.

The ASTM compilation (Ref. 4) describes a very similar method. The lower detection limit is about 1 pCi/liter. Both the APHA and the ASTM methods are based on a technique developed at Idaho Falls (Ref. 36) and also described by Goldin (Ref. 37).

Another chemical method is described in the USPHS compilation (Ref. 38). Here radium is coprecipitated with $BaSO_4$ from a solution containing EDTA; the precipitate is converted to carbonate and dissolved in HNO_3. Radium daughters are extracted into thenoyltrifluoroacetone, and Ra-$BaSO_4$ is reprecipitated for counting.

A quite different method has been developed by Duquesne et al. (Ref. 39). Here the final sulfate precipitate is suspended in ethanol together with a powdered scintillator, ZnS(Ag), and this mixture is filtered and dried for counting with a photomultiplier. Sensitivity below 0.1 pCi/liter is claimed, and by studying the alpha activity as it evolves in time the $^{224}Ra/^{226}Ra$ ratio can be roughly determined.

Kelkar and Joshi (Ref. 40) describe a system which is similar but even simpler. After a one-liter sample is filtered, HCl and $BaCl_2$ are added. Radium, lead, and polonium are coprecipitated with 36 M H_2SO_4, and 400 mg of ZnS(Ag) are added while stirring. A Whatman 42 filter then picks up the sulfates and the ZnS(Ag) together; the filter is dried under an infrared lamp for two minutes, and counted for 30 minutes. Chemical yields exceed 95%, and concentrations as low as 1 to 3 pCi/liter can be determined. This method, though less sensitive than the more sophisticated techniques, is quick and economical.

To summarize, there are a variety of chemical methods which take advantage of coprecipitating radium with barium, as sulfate or carbonate, to separate it from other alpha-emitting elements (principally daughters of the various radiums). After successive purifications in one of several chemical media, the methods either count the radium salt in an internal gas proportional counter, or use ZnS(Ag) and a photomultiplier tube for scintillation counting.

In any of the methods which use alpha counting, the substitution of alpha spectroscopy can result in a direct determination of radium isotope ratios. However, resolution is a key consideration. Typical resolutions (± half-width) that can be obtained in various kinds of alpha spectrometers are about ±15 keV with surface-barrier detectors; ±20 keV with pulse ion chambers; and ±50 keV with gas proportional counters. Liquid scintillators (±150 keV) and solid scintillators (±200 keV) are poorer. Any of these systems can resolve ^{226}Ra (4.60, 4.78 MeV alphas) from ^{223}Ra (5.54, 5.61, 5.71, 5.75 MeV) and ^{224}Ra (5.44, 5.68 MeV). However, separating these latter two from each other is more difficult because the energies are so intermingled.

2.222 Radiochemistry with Counting of Radium Daughters

In the following section those methods by which radium daughters (other than radon gas) are counted after radiochemical separation will be summarized.

One technique, in the HASL Manual (Ref. 41), separates lead-212 in urine and measures the alphas from bismuth-212 and polonium-212 after equilibration. This technique is specific for *radium-224* (the precursor of ^{212}Pb). In another HASL technique applicable in urine or water, Ra-BaSO$_4$ precipitate is stored for buildup of Rn-222, Po-218, and Po-214, which are measured in equilibrium using a ZnS(Ag) disk phosphor and a photomultiplier. Petrow and Allen (Ref. 42) describe a specific determination of radium-223 in uranium mill wastes, from which it is separated together with a lead carrier. After radium-223 is separated from the lead carrier, it is stored for 3 hours to allow ingrowth in solution of the radium-223 daughter, lead-211 (36.1 minutes, 1.39 MeV max. β). The lead-211 is then extracted from solution into dithizone. Interference from lead-214 (daughter of radium-226) is minimized by boiling the solution during the 3 hour period, in order to purge the precursor of lead-214, 3.8-day radon-222. Loss of radon-219 (precursor of lead-211) during the boiling is stated not to occur because of its short half-life (4 seconds). The α-activity counted derives from bismuth-211 (6.62 MeV daughter of lead-211).

A similar procedure can be used to determine *radium-224*. The separated radium sample is aged for 16 - 24 hours to obtain lead-212 ingrowth from ^{224}Ra. Lead-212 (10.6 hours) is separated from lead-211 (36.1 minutes) by aging of the lead extract for 3 - 4 hours before beta-counting.

Petrow and Allen (Ref. 42) also describe a method for *radium-228* by separation and counting of its daughter, actinium-228. To avoid any interference, the radium sample must be purified of ^{227}Ac before ^{228}Ac ingrowth. This is achieved by using lanthanum hold-back carrier prior to the radium-sulfate precipitation. After ^{228}Ac ingrowth from ^{228}Ra, the sample is beta-counted in an internal gas proportional counter.

In summary, several chemical methods have been briefly discussed which selectively determine one of the radium isotopes by the chemical or physical properties of its daughter(s). These analytical methods are useful only in restricted circumstances, but they are a valuable tool when detailed knowledge of the various radium isotopic ratios is required.

2.223 The Radon Emanation Method

This is the method of choice for most laboratories doing large numbers of radium analyses. Procedures are described in reference 44, Handbook of Radiochemical Analytical Methods(EPA-680/4-75-001), and in Standard Methods (Ref. 5), Section 706.

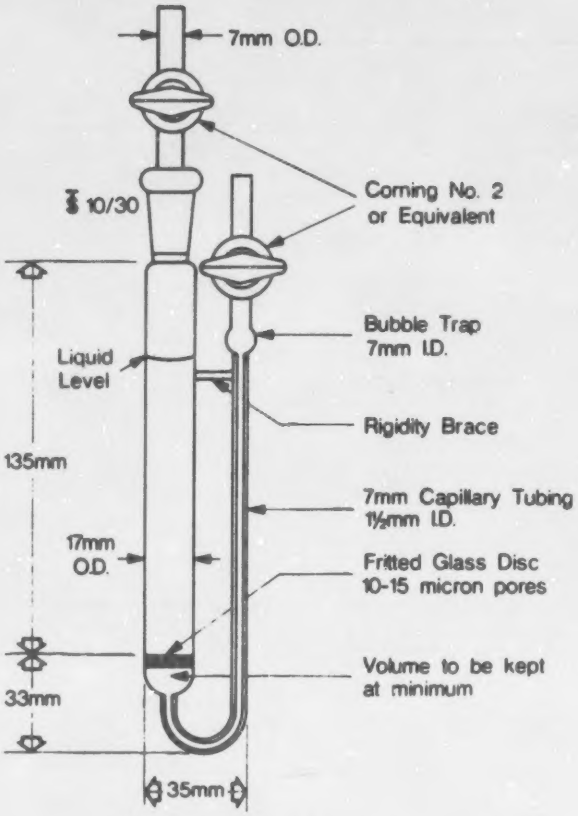

FIGURE 6. Emanation tube (Bubbler). (Ref. 44, p. 45).

In the EPA method for water, radium is concentrated and separated from sample solids by coprecipitation with lead sulfate, the lead-radium sulfate reprecipitated as carbonate, and the carbonate re-dissolved in dilute nitric acid. The solution is transferred to a radon *bubbler* (Fig. 6) and allowed to ingrow for 28 days.

In the Standard Methods procedure radium is co-precipitated with barium as the sulfate, the precipitate treated to remove silicates if they are present, and to decompose any insoluble radium compounds. The solution is then fumed with phosphoric acid to remove SO$_3$, dissolved in HCl and placed in a bubbler which is closed and stored for a suitable period (several days to 4 weeks) to allow for the ingrowth of radon. The bubbler is then connected to an evacuated system (Fig. 7) and the radon gas removed from the liquid by aeration, dried with a dessicant, and collected in a counting chamber. The latter consists of a dome-topped scintillation cell coated on the inner surface with a silver-activated ZnS phosphor. The bottom of the chamber is a transparent window. During counting the chamber rests on a photomultiplier tube.

After equilibrium is established between radon and decay products (~ 4 hr), the subsequent count obtained is related to radium-226 standards which have been treated similarly.

Aged helium, nitrogen and air have all been used to purge radon from the solution for transfer to the counting chamber. The EPA method calls for compressed air, held for 90 days before use. Helium, however, gives the best results with respect to both yield and scintillation pulse heights (Ref. 5).

2.224 Summary and Conclusions

In general, environmental activity levels requiring measurement are very small, and the measurement techniques correspondingly sophisticated. Most routine measurements today use either an emanation technique or radiochemical separation followed by alpha counting. Each of these types of measurement can be performed sensitively and accurately enough to determine the radium isotopes at their naturally-occurring activity levels in the environment. Unfortunately, each suffers from drawbacks: The radiochemical methods require exacting analytical procedures; the emanation techniques are time-consuming and the apparatus cumbersome and relatively costly.

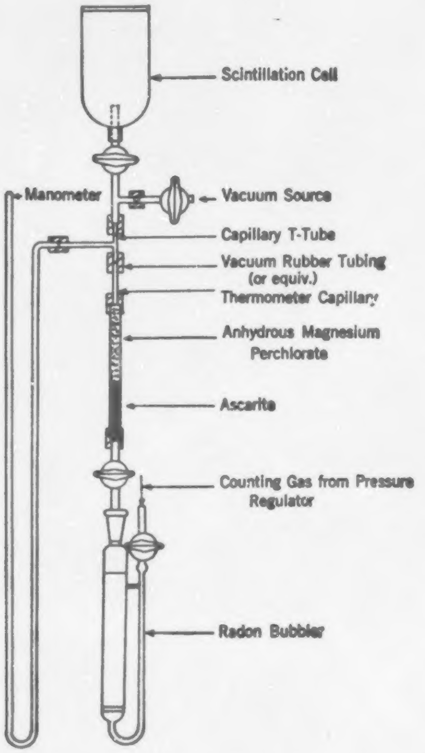

FIGURE 7. De-emanation assembly (Ref. 5, p.667)

However, in the overall picture of radionuclide measurement capabilities in environmental media, radium measurements appear to be in a reasonably sound position. The quick screening (gross-alpha) measurement techniques for public health protection are adequate, and radium levels can seldom be expected to increase suddenly to the danger point where both time and accuracy would be essential. Thus the present methods, though time-consuming, are probably adequate for the task of routinely monitoring environmental samples for radium content.

2.3 Calibration Sources

These will be discussed in greater detail in the following section. The U. S. National Bureau of Standards has developed a set of standards with radium-226 content in the picogram to nanogram range, contained in flame-sealed glass ampules (Ref. 43). These *solution standards for radon analysis* are for use in calibrating an entire counting system.[a]

2.4 Standards

General information on radionuclide standards is provided in two NBS publications (Ref. 50 and 51). Standards for elements commonly encountered in wastewaters may be obtained from the National Bureau of Standards (Ref. 43) and from Amersham/Searle Corporation in the U. S., from the IAEA Vienna (Austria), the Radiochemical Center at Amersham (England), and Centre Energie Atomique (CEA), Saclay (France). Other commercial sources of standards will be listed in the appendix. Table 13 is a list of standards made available by the NBS after April 1974. A more complete and recent listing is provided in Appendix 3.

3. Detectors

Radiation detectors are an essential stock-in-trade of the laboratory engaged in

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[a] See p. 60, Ref. 43a; p. 16 in Ref. 43b, and NBS brochure dated Aug. 1976 (43c).

TABLE 13. NBS Calibration Standards Issued After April 1974*

Radionuclide	Gamma-Ray Energy (MeV)	Approximate Activity (ntps) at Time of Calibration (month, year)	Approximate Weight of Solution (grams)	Accuracy %	SRM No.	Price Per Sample
Cadmium-109 (point source)	0.088	4 to 7 × 10^3 γps 5/74		1.9	4202B	100.00
Iron-55 (point source)	0.0059	200 to 400 of Mn K-x-rays per steradian		3.0	4260	100.00
Americium-243 (solution)		8 × 10^3 dpm/g	2	< 3%	4332	100.00
Americium-243 (solution)		2 × 10^2 dpm/g	5	< 3%	4333	100.00
Cadmium-109 (solution)	0.088	10^5 γps/g 5/74	5	1.9	4219	100.00
Carbon-14 (solution)		4 × 10^5 ntps	5	1.0	4245	100.00
Carbon-14 (solution)		4 × 10^4 ntps	5	0.9	4246	100.00
Carbon-14 (solution)		4 × 10^2 ntps	5	1.1	4247	100.00
Plutonium-239 (solution)		3 × 10^3 dpm/g	2	< 3%	4330	120.00
Plutonium-239 (solution)		3 × 10^2 dpm/g	2	< 3%	4331	120.00

*See Appendix for a more complete listing of calibration standards available from NBS as of June 1975.

radionuclide analyses,[a] since they are used universally for all manner of radiation measurement: 1) gross activity, 2) post-chemical-separation counting of individual nuclides, or 3) multiple nuclide determinations in a single sample. What follows is of necessity a brief treatment covering considerations relevant to the detection of radiation in water and the reader is encouraged to consult LBL-1, Volume 3, RADIATION, for more in-depth coverage of this subject.

The type of radiation to be measured will naturally affect the detector selected--as will the energy of radiation emitted. These factors also influence the chemical separation scheme employed (see this chapter, under D2. Analysis for Radionuclides). A detailed discussion of specific instrumentation is presented in volume 3, RADIATION, of this series.

Alpha particles (He^{++}) are emitted by a large number of radionuclides present in nature, most of them elements with atomic weights greater than lead (Pb). Since alphas are highly ionizing, little pulse amplification is required in their detection and measurement in a gas ionization chamber (see Table 14). However, because of alphas' short range, samples for α-detection must be ultra-thin and very uniformly distributed on the planchets to be counted. An alternative approach involves the

TABLE 14. Radiation Detectors (Ref. 24)

Detectors	Radiation
Gas ionization[a]	
ionization chamber[b]	α(internal), γ(high pressure)
proportional[b]	α(internal or thin window), β, X (high Z gas)
Geiger-Müller	α(internal or thin window), β
Scintillation[a]	
liquid	
organic[b]	α, β
Cerenkov	β
solid	
organic	α, β
NaI (Tl)[b]	γ
CsI (Tl)	α, γ
ZnS(Ag)	α
Semiconductor junction[a]	
Si[b]	α, β
Ge(Li)[b]	γ
Others	
photographic film	α, β, γ
cloud chamber	α, β
calorimeter	α, β

[a] Gas ionization counting depends on the formation of ions within an electric field as a result of interaction of radiation with counter gases. The ions are collected on electrodes and measured as pulses with a counter, as current with an electrometer, or as rate of drift with an electroscope. Scintillation counting depends on the stimulation of light emission by the radiation in the scintillator. The light flashes are converted to pulses in a phototube, and the pulses are amplified and counted. Semiconductor junction detectors are the solid analogs of gas ionization detectors. Electrons and holes freed from valence bonds by radiation move to the electrodes within the electric field in the solid, and the pulses are amplified and counted.

[b] Used for spectrometry.

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[a] Very long-lived radionuclides (Th, U) have such low specific activities, that standard analytical chemistry is used in their determination rather than counting techniques.

measurement of "infinitely" thick samples to avoid counting errors due to the variations in sample thickness.

α-*Particles* may be counted using ionization chambers, ZnS(Ag) scintillators or low voltage proportional counters, all without interference from β- or γ-radiation. More recently silicon surface barrier detectors have been employed for both α- and β-detection. Table 14 lists most commonly used detectors. As a consequence of their short range, α-samples must be situated within the gas counters, or separated from them by very thin windows. Events may be recorded by means of a) a counter, b) film tracks, c) an electrometer or electroscope or d) a spectrometer.

β-*Particles* are emitted over a continuous range of energies, from zero to some maximum value characteristic of the particular nuclide. It is this latter value which normally is reported in the energy literature. Beta-counting is the preferred method of gross measurement of radioactivity since nearly all fission products and most thermal *neutron activation* products emit β-radiation in addition to other kinds of radiation.

Positrons, or *positive electrons*, are emitted by those radioisotopes of lesser atomic weight than their stable counterparts. As with β-particles, the positrons also appear as an energy continuum.

Conversion electrons are monoenergetic species sometimes emitted instead of γ-radiation.

All three radiation species (betas, positrons and conversion electrons) may be detected using the same instruments.

Above 0.1 MeV, betas are more penetrating than alphas but generally there is some absorption of betas within the sample as well as in the material located between detector and sample. For low energies and thick samples, a major β-fraction may be absorbed.

Detection of β-particles is generally via gas counters operating in the Geiger-Müller and proportional voltage range, photographic film, or liquid/solid scintillation counters (see Table 14). Silicon detectors are also widely used for betas. In order to eliminate α-interference, betas with energies > 0.1 MeV are subjected to external counting with detectors fitted with windows of suitable thickness. At 3.5-4 MeV, further discrimination between alphas and betas occurs, β-radiation generally falling below 3.5 MeV, α-radiation, above this range. Gamma rays do not interfere appreciably when gas detectors are used. This also holds for small liquid/solid detectors. In the case of very weak betas such as those obtained from tritium, the sample is best counted by dissolution in a liquid scintillation counter or, where more convenient, by introducing the gaseous form of the nuclide into the gas counter.

Gamma and *x-rays*, because of their low specific ionization, are not counted with high efficiency, in α- and β-(gas ionization) counters. Table 15 indicates that these are

TABLE 15. Range of Radiations in Aluminum, mg/cm^2 [a] (Ref.24)

Energy, MeV	Range of alpha particles [d]	Range of beta particles [d]	Half-thickness for gamma and X-rays [b]
0.01	— [c]	0.2	27
0.02	—	0.7	200
0.05	—	4.0	1,600
0.10	—	13.0	4,000
0.20	—	42.0	5,800
0.50	—	170.0	8,000
1.0	—	420.0	12,000
2.0	—	920.0	16,000
3.0	—	1500.0	20,000
4.0	4	2000.0	22,000
6.0	7	— [c]	— [c]
8.0	11	—	—

[a] For specific gravity of 2.70, 2700 mg/cm^2 = 1.0 cm thickness.

[b] Thickness needed to reduce the gamma and X-ray intensity by one-half.

[c] Values not listed if radiations are not commonly emitted at indicated energies

[d] From Ref. 34.

relatively penetrating radiations. They interact with matter by virtue of their *photoelectric effect*, and by *Compton scattering* and/or *pair production*. Peaks due to photoelectric effect and pair production may be specifically identified and quantified by means of γ-ray spectrometry (Ref. 24).

At photoelectric peak energies, good resolution is obtained as a result of total absorption, but Compton scattering of higher energy photons may hamper the measurement of lower-energy peaks exhibited by other radionuclides present.[a]

Above 0.1 MeV γ-radiation may be detected using large scintillation crystals or gas-filled ionization chambers operating at high pressures. Cylindrical crystal detectors of NaI(Tl) about 10 cmH × 10 cm in diameter are commonly used as detectors in this energy range.

Lower energy γ-radiation --0.02 to 0.1 MeV--is generally detected with thinner versions of scintillating crystals, or via Ge(Li) detectors. X-radiation in the 0.01 MeV range is detected by means of xenon-filled proportional counters (Ref. 24).

High energy γ-radiation presents no difficulty, since large samples may be measured with negligible self-absorption. Alpha- and β-particle interference is eliminated by their absorption in a low atomic number substance (e.g., Al, Be, or a plastic).

4. Radioactive Wastewaters

Radioactive wastewaters present a special analytical problem, since they usually contain proportionately larger quantities of inactive suspended and/or dissolved solids than does fresh water. Furthermore, much of the activity may be in the solid phase which must first be solubilized for the effective use of carriers. The presence of a high level of fixed solids is often a source of interference in radioanalytical procedures. Distribution of commonly encountered radionuclides between the solid and liquid phases in wastewaters is shown in Table 16.

The presence of complexing agents in wastewaters may further affect the behavior of radionuclides in these media. Thus the radioiodine from medical sources may be in a complex, organically-bound form rather than in the simpler molecular or ionic (iodide) states in which it normally occurs in fission products from spent nuclear fuels. Similarly, tritium from the manufacture of luminous products may also be present in an organically-bound form. The strontium-90 titanate waste from a radioactive heat source is in a much less soluble form than its counterparts in most other Sr-90 wastes; and, after processing in uranium mills, thorium and uranium daughter products are frequently present in the forms of inorganic complexes rather than as oxides.

Information on the behavior of radionuclides, the chemical composition of wastes, and the radioisotopes currently in use may be obtained from references 45 and 46. For more detailed information on radionuclide analysis of wastes and environmental samples, consult references 4, 47, 48 and 49.

E. INSTRUMENTATION

In the following section, counting instruments employed in radionuclide detection and measurement will be described briefly. For a more detailed treatment of this subject, the reader should consult volume 3 (RADIATION) of this series.

Operating Principles

Both *Geiger-Müller* and *proportional counters* are activated by the ionization of an indicator gas, triggered by the absorption

TABLE 16. Distribution of Common Radioelements Between Solid and Liquid Phases of Wastewaters[†]

In Solution	HCO_3^-, Co, Cr, Cs, H, I, K, Ra, Rn, Ru, Sb, Sr
In Suspension	Ce, Cs, Mn, Nb, P, Pm, Pu, Ra, Sc, Th, U, Y. Zn, Zr

[†] Adapted from Ref. 5.

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[a] A more detailed discussion of interferences is found in LBL-1 Vol. 3 RADIATION, Section R-XRA GAM (Ref.1C).

of energy produced during the radioactive decay of nuclides. Electrons produced in the counting chamber during ionization events are collected at the anode, and the resulting signals amplified and recorded.

Collected charge may be measured as pulses with a counter, as current with an electrometer, or as the rate of drift, using an electroscope.

In *scintillation counters* a radiation event excites a *phosphor* and the resultant photon production is detected by means of a photomultiplier tube which converts the amplified photon signals to electronic form. Phosphor screens of silver-activated zinc sulfide [ZnS(Ag)] and thallium-activated sodium iodide crystals [NaI(Tl)] are used for α- and γ-counting.

1. Counters: Types and Applications

1.1 Internal Proportional Counters (IPC)

Since the internal proportional counter (IPC) accommodates counting pans within its chamber, all α- and β-events (and a fraction of the γ-emissions) will be recorded at the β-operating voltage. From geometric considerations for a very thin ("weightless") sample, it is assumed that one-half of the radiation is emitted in the direction of the pan itself with appreciable back-scattering, primarily of β-radiation, occurring into the gas. Scattered α-radiation contributes no more than 1 or 2% to the signal. Thus, well over 50% of the β-events and just over 50% of the α-events will be recorded in the IPC (see Ref. 5). Hence, IPCs are applicable to the measurement of α-activity at the appropriate voltage (*α-operating plateau)* and the sum of α- and β- activities at the *β-operating plateau* without regard to the radionuclide source(s) of these emissions.

IPCs generally include the following components in addition to the counting chamber: a preamplifier, scaler equipped with a high voltage power supply, timer and recorder. Counting gas and accessories are specified for a particular instrument. General experimental procedure is described in reference 5, but will vary with the instrument as regards sensitivity adjustments and α or β- plateau voltage (i.e. voltage setting where a constant counting rate is obtained).

1.2 Geiger Müller Counters

The Geiger-Müller counter takes a variety of forms, depending on its intended use. Thus, to detect β-rays, it may be equipped with a thin wall or end window. For alphas and very weak betas, it may be made with an open window and provided with continous gas flow. For energetic gamma, the outer electrode may be constructed of a heavy metal element to enhance secondary electron production and thus improve response. Two of these variations-namely the G-M end window and the thin window proportional counters-are discussed in the following two sections.

1.21 Geiger-Müller End Window (GMEW) Counters

These counting tubes are generally rugged and have the advantage of stability. Samples are mounted so that they are separated from the mica window by an air gap of from 5 to 15 millimeters. This is sufficient to eliminate most α-radiations and the weaker betas which will not be transmitted into the counting chamber under these conditions. The volume of the aqueous sample is limited by the G-M tube diameters -- generally of the order of 2.5 centimeters -- which in turn limits pan size, thus indirectly restricting liquid volumes. This renders G-M tubes unsuitable for detection where the radiation source is unknown and may be of low intensity. However, they serve admirably when used to measure purified samples of nuclides or of tracers.

1.22 Thin Window Proportional Counters

Thin window counters are tubes of ~ 5 cm diameter with thin Mylar windows ($<250\mu g/cm^2$). They have counting efficiencies which fall between those exhibited by standard G-M tubes and IPCs, and although they are about half as sensitive as internal counters, their performance with α-emitters is satisfactory. These counters exhibit considerable operational stability and are less affected by moisture or insulating surfaces than are IPCs. Their chamber diameters are considerably larger than for the standard G-M counter ($\geq$60 mm), so that sample mount diameters may be correspondingly large ($\geq$50 mm). In all, these large diameter thin window counters out-perform their standard G-M counterparts.

Figure 8 shows typical counting rate-anode voltage curves for an internal proportional counter (a,b) and a Geiger-Müller End Window counter (c).

1.3 Low Background β-Counters

These counters are designed primarily for β-emitters having a maximum β-energy > 0.3 MeV. Low background β-counters are useful for measurements in the 0.1-50 pCi range, although it is possible to count up to 1000 pCi with these instruments. Attenuation of high energy betas is negligible, since the detector window is < 1.0 mg/cm^2. Sample pan diameters are small--less than the window area, and counting efficiencies in the 30-55% range are obtained for intermediate range β-radiation.

Counters in this category generally use helium-isobutane or similar gases which operate

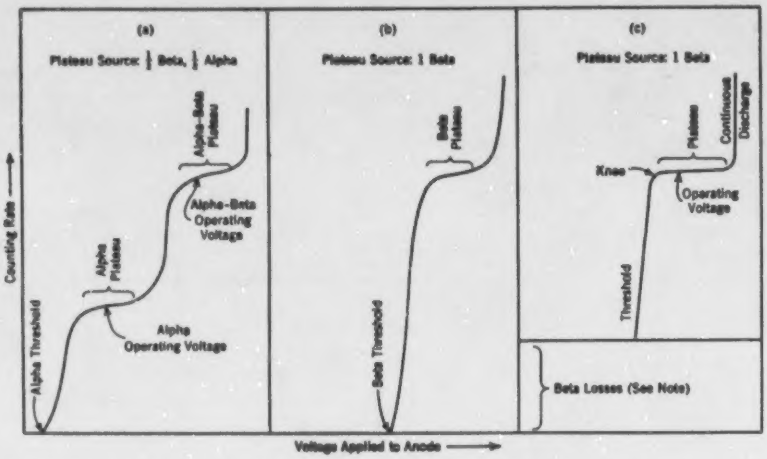

FIGURE 8. *Shape of counting rate-anode voltage curves. Key: (a) and (b) are for internal proportional counter with P-10 gas; (c) is for end-window Geiger-Müller counter with Geiger gas (Note: Beta losses are dependent on energy of radiation and thickness of window and air path). (Ref. 5, p. 638).*

in the Geiger region. Resolving times of G-M counters are normally between 100-400 μsecond. Thus, for high sample counts, the data must be corrected for counting losses.

For instruments with a counting rate of ≤ 1 cpm, detectors are normally shielded (Pb or steel) and equipped with an anti-coincidence device.

1.4 α-Scintillation Counters

Impure ZnS crystals *phosphoresce (scintillate)* in the visible region when bombarded by α-particles. Silver impurities in the sulfide enhance phosphorescence, and nickel ions (Ni^{++}) shorten the time span. Thus, together, these two impurities increase the efficiency of scintillation.

In the α-scintillation counter a phosphor detector is coupled to a photomultiplier, an amplifier-discriminator, a scaler, and a high voltage supply. If the phosphor is not provided with a light-focusing optical system, the photomultiplier tube window diameter should exceed that of the sample.

In the usual procedure the phosphor is placed in close proximity with the α-emitter and oriented so that the photomultiplier tube picks up the photon energy pulses and converts them to electronic signals which are then amplified and recorded on a scaler.

1.5 Liquid β-Scintillation Counters

The basic principle is discussed under Section 1.4 above, the difference being that the sample is mixed with an organic liquid scintillator and the light produced is detected and amplified by one or more photomultipliers.

These counters are particularly useful in the measurement of low energy β-emitters (e.g., tritium, carbon-14), since losses due to self-absorption are eliminated. For high-energy betas, efficiencies can approach 100%; for tritium, where the low energy betas go undetected,[a] the efficiency is much lower. As a means of reducing dark current background effects, liquid scintillation counters may be equipped with two photomultipliers in coincidence.

Generally, liquid scintillators are provided with two channel analyzers, at least, so that the simultaneous measurement of more than one β-emitter is possible, provided that the energy maxima differ by a factor of 3 or more.

1.6 Coincidence Counters

When radionuclides simultaneously emit two or more kinds of radiation, *coincidence counting* may be used for further distinction and identification of species by combining γ-ray spectrometry with coincidence counting

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[a] Low energy betas of ^3H are at the *dark current* level of the PM tube itself, and therefore eliminated in the discrimination process to reduce background *noise*.

(Refs. 1c, 5 and 24). Two or more suitable detectors are connected so that only the coincident radiations produced within a predetermined energy range are recorded. The same instrumentation may also be used for the detection of non-coincident radiation.

One elegant application of the coincidence technique is *multidimensional photon-photon coincidence* spectrometry in which energy coincidences are displayed in two dimensions, and intensity in a third. The technique utilizes an analyzer equipped with several thousand channels.

2. Gamma Spectrum Analysis

Gamma ray spectrometry is based on the interaction of γ-radiation with sensitive detectors (e.g., NaI(Tl), Ge(Li)) to produce pulses of radiation with intensities proportional to the incident γ-photon energies. It is possible to analyze many radionuclide samples using these detectors in conjunction with multichannel spectrometric methods (Ref. 24).

Except in the case of complex spectra resulting from radionuclide mixtures, γ-ray spectrum analysis requires minimal chemical separation. However, the measurement of radionuclides with photon energies of <0.1 MeV entails appreciable uncertainty (Ref. 5). A further disadvantage of the method is that it cannot be used to measure nuclides which do not emit γ-radiation.

Of the two detectors commonly employed, Ge(Li) has the better resolution by an order of magnitude (~2 keV vs 50 keV at 660 keV), and thus does a more precise job of identifying γ-radiation energies. Consequently it can cope with more complex radionuclide mixtures.

However, the NaI(Tl) detector is generally more efficient since it contains iodine—an element of heavier atomic weight—and can also be made much larger than the Ge(Li) detectors. Also, the latter operates at liquid N_2 temperatures, whereas NaI(Tl) is operated at room temperature.

2.1 Procedure

The sample is mounted under reproducible conditions with regard to the following parameters: geometry, scattering materials, sample internal radionuclide distribution, shape and density. The required precision determines the number of counts per channel to be accumulated and varies with the sample. After subtraction of background the net spectrum is compared with appropriate standard spectra measured under identical conditions as to peak energies, shape and count rate.

Identification of radionuclides which emit γ-radiation may be further confirmed from observations of the relative intensities of γ-radiations decaying with the same half-lives. By repeated counting, the decay of the shorter lived nuclides may be sorted out from the longer lived species, initially obscured by the γ-ray spectra of the short-lived nuclides.

3. Solid-State (Surface-Barrier) Detectors

The introduction in the early 1960's of solid state detectors for high-resolution particle detection revolutionized the state-of-the-art in many fields of research. In the case of alpha particles, the short range necessitated development of a detector with its sensitive area almost entirely on the surface. (This is in contrast to the case of gamma-ray detection, where the most significant advances were directed toward detectors with larger and larger volumes.)

The *surface-barrier detector* is now the solid-state detector type most commonly used for alphas. The most striking advances, however, were in the field of gamma spectroscopy, where the resolution of previous techniques (such as NaI(Tl) scintillators) was increased by large factors. For beta spectroscopy, the advances have been nearly as great, but the importance of the new technique here has been far overshadowed by its use in gamma spectroscopy. Partly, this is due to the lack of need for very precise energy resolution in much of beta spectroscopy research, because of the wide energy spectrum. However, for conversion electrons, this technique will provide very high selectivity for the mono-energetic line.

The range of betas is sufficiently short so that they can be totally absorbed in solid state detectors of quite modest dimensions, silicon being nearly identical to aluminum in its stopping power for betas. Two problems are important, however; first, some backscattering will occur, resulting in a degradation of energy resolution on the low-energy side for a fraction (several percent) of the incident betas. This effect is not as serious for silicon as it would be for a high Z scintillator, e.g., NaI(Tl), because of silicon's low atomic number. Nevertheless, it contributes to the difficulty in measuring low-energy spectra in the presence of high-energy betas.

Second, a premium is placed on making the dead layer at the surface of the detector as thin as possible. For this latter reason, detectors with sensitivity almost directly at the surface have been developed. These are the *silicon surface-barrier detectors*. A typical silicon surface-barrier detector is a cylindrical diode with a very thin p-type silicon layer on the face of an n-type silicon wafer. Above the p-type layer, a thin surface of gold (thickness $\leqslant 0.02$ microns, $\leqslant 40\ \mu g/cm^2$), provides the negatively biased electrical contact; the positive bias is made through some metal contact (e.g., aluminum) on the back of the *n*-type silicon. The gold layer also serves as a means of protecting the active elements from contamination. Detectors with depleted depths from about 50 microns to a few millimeters are now commercially available, with surface areas from a few to several hundred mm^2.

Solid state detectors using silicon or germanium have several distinct advantages over gas-filled detectors. The two primary advantages are:

1) For a given amount of energy lost through ionization, the number of charge carriers (corresponding to ion pairs in the gas) is greater by a factor of as much as 10. This decreases the statistical fluctuations in the ion collection process, and is the main reason for the superb resolution.

2) Collection time in the nanosecond range makes fast time resolution possible; this is due to the high mobilities and short distances involved.

3) When semiconductor purity is high, recombination effects are less important than for a gas; this is particularly important when ionization is locally dense, as is the case with alphas (or fission fragments).

Among the difficulties associated with surface-barrier detectors are the following:

1) The detectors are fragile and require careful storage and handling.

2) The output signals are very small, and electronic amplification is required.

3) Noise in the detector/amplifier system is often the dominating characteristic around which a system is designed.

4) The detectors can become contaminated, and once this happens decontamination is essentially impossible.

Detection efficiency is in the range of 100% for alphas or betas incident on the sensitive area of the detector. Backscatter loss is the dominant degrading effect for betas. For alphas the range in silicon is exceedingly short-- 18 μ at 4 MeV and 60 μ at 9 MeV--and backscatter is not a factor. Furthermore, backgrounds from external sources (e.g., cosmic rays) or from detection of gamma rays, are very small because of the small size of a typical detector.

Energy resolution and sensitivity are the main reasons for the choice of a surface-barrier detector. Although broadening of a monoenergetic peak due to random noise fluctuations in the detector and/or preamplifier is an intrinsic limitation in many applications, this is not a significant effect for alphas: the ultimate resolution here (typically about 15 keV full-width-half-height) is limited by imperfect charge collection and by variation in the energy lost in the dead initial layer.

For betas, the broadening from backscatter losses and from variations in the energy lost in the dead initial layer constitute limitations, and line widths of about ±5 eV for electrons in the 1 MeV region are typically obtained in the best systems.

F. ERROR: SOURCES AND CONTROLS

In the preceding two sections D3 and E the most commonly used instruments for radionuclide analysis in water were briefly described. Here the analytical application will be examined for limitations, sources of error and analytical quality control efforts to improve data reliability.

1. Background and Environmental Factors

Generally counting instruments exhibit *background* count rates attributable to instrument noise in the detector and cosmic sources of radiation. In addition, there may be some contamination present, either from room construction materials or from proximity to x-ray equipment and to samples containing radionuclides. By the judicious selection of construction materials for the counting room and the use of heavy metal shielding (e.g., several inches of Pb), the background due to various radiation contaminants *external* to the counter may be considerably reduced. *Internal* background is kept to a minimum by minimizing radioactive contaminants within the counting chamber.

Another source of counting error encountered in earlier instruments stems from recording as apparent radiation events those specious signals which are in reality due to instrument *noise*. Such noise may stem from a variety of electronic problems e.g. the variation in line voltage, transients, a faulty circuit, current leakage due to high relative humidity or a gain adjustment which results in excessive instrument sensitivity. This noise component may be minimized by the use of transient filters and constant voltage transformers, by air-conditioning counting rooms and insuring that they are free of dust and fumes, and by adhering to the manufacturer's recommendations with respect to gain adjustment range. With the introduction of solid state circuitry many of these problems have been eliminated. For some limitations of the latter systems see section E.3: Solid State (Surface Barrier) Detectors.

Background counting may be further lowered and instrument stability improved by the use of several inches of concrete in ceiling, floor and walls of the counting room. It should be noted that certain natural building materials (some granites, sands and shales) have considerable natural activity and will thus increase the instrument background if used in counting room construction.

Previous background sources of error discussed may lead to high counts. Another source of counting error, this time leading to low values, may arise from sample preparation. Precautions must be taken to avoid reduced counts as a result of electric field distortions in the counter due to contamination of sample or pan with airborne dusts, water vapor or solvents. Insulating surfaces may also interfere with counting.

In order to insure accuracy of the data and minimize error, it is necessary to have a system of *quality control*. Precision values for reporting analytical results are provided by the quality control data, which also alerts the analyst when any corrective action is required. Usually the quality control system provides the following information: a) daily log of count standards for all detectors in use; b) daily background monitoring. For count rates which are too low to permit a sufficient daily count accumulation, background may be determined by overnite or over-the-weekend measurement. c) When significant changes have been made in a detector, or when a new one is installed, count calibration standards must be established. d) Knowns, replicates and blank samples must be analyzed, and e) all quality control data must be recorded.

Appendix 5 includes a plot of error as a function of total count and length of count, two error nomograms, and a brief mathematical statement of the statistics of counting.

2. Limitations of Detectors

Since the supply of calibrated instruments covering a requisite radionuclide range is likely to be strictly limited in most laboratories, it is clear that detectors must be chosen judiciously to satisfy the specific analytical needs of the laboratory in question. Radiation detectors are utilized in a broad variety of ways, depending primarily on the intent of measurement. Thus, *gross activity* may be measured to ascertain the degree of compliance with regulations; or, it may be determined to provide information as to the size of aliquots required for accurate determination of specific radionuclides. Gross activity may also provide a check on separate nuclide analyses for material balance.

By subjecting the water sample to a more detailed instrumental examination, gross activity analysis may be further utilized to provide a clue as to the radionuclide composition of the sample. Thus: *a)* the *nature* of the radiation *(s)* may be determined via a suitable detector and/or appropriate filter(s); *b)* radiation *energies* ascertained, either spectrometrically or by means of a plot of the variation in count rate with thickness of the absorber; *c)* the sample *half-life* may be determined; *d) genetic* information obtained from growth and decay curves, and *e) intensity* and *coincidence* relationships of the emitted radiation established. Water sample volumes required for gross activity measurements are determined by sensitivity requirements for each individual case and may be calculated from equation (f) in Table 3.

In the last analysis, however, even such an intensive sample examination for gross activity has its limitations. Some nuclides may be lost during preparation of the sample for counting; others may escape detection as a result of interfering contaminants, both stable and radioactive. By performing chemical separations preliminary to counting, the latter losses are minimized, as are the uncertainties associated with the identification of nuclides purely by their radiation characteristics.

Procedures a) through e) discussed in connection with gross activity measurement on the original water sample are equally applicable to the chemical isolates. In the latter case they are used to 1) determine the activities (and therefore the amounts) of individual radionuclides in a mixture; 2) to confirm analytic results of gross activity, and 3) to ascertain the degree of separation from interfering radionuclide contaminants under experimental conditions. Where a preliminary chemical separation has been carried out, detectors are used to derive quantitative data on nuclide concentrations from a number of variables; namely, 1) *counting rates* and 2) *efficiencies*, 3) *carrier yields*, and 4) *sample volumes*. At each step, and for each variable, limitations of human and instrumental origin determine *minimum detectable levels* (MDL) attainable. In Table 17, method capabilities for specific radioanalytic procedures are listed for three parameters; sample volume, counting efficiency and instrument background (Ref. 52, Appendix A; p. 41)

3. Quality Control: Interlaboratory Method Studies

The Quality Assurance Branch of the EPA conducts formal interlaboratory studies among EPA laboratories to evaluate methods selected by EPA for its method manuals such as *Methods for Chemical Analysis of Water and Wastes*. However, other federal, state, local, university, and industrial laboratories are accommodated in these round-robin studies as their interest becomes known. The studies carry deadlines and conclude with reports distributed to all participants. In these reports the laboratories are identified only by code number. Announcements of new studies are made in the *AQC Newletter* published by the EPA (Ref. 56).

The Quality Control (QC) samples are furnished without charge to interested governmental, industrial, commercial, and private laboratories for their within-laboratory quality

TABLE 17. Method Capabilities*

	Parameter			2σ MDL pCi/1	
	Sample Volume	Counting Efficiency %	Instrument Background	1000 min count	60 min count
Gross beta activity	100 ml	39	1.0 c/m	1.2	4
	250 ml			0.5	1.8
	500 ml			0.3	1.0
Gross alpha activity	100 ml	41	0.2	0.5	1.8
	250 ml			0.2	0.8
	500 ml			0.1	0.5
^{134}Cs	1000 ml	31	1.2	0.2	0.6
^{137}Cs	1000 ml	34	1.2	0.2	0.5
^{131}I	2000 ml	32	1.0	0.1	0.3
Radium-precipitation	2000 ml	40	0.5	0.04	0.15
^{226}Ra-Rn emanation	1000 ml	70	0.03	0.01	0.04
^{228}Ra	2000 ml	40	1.5	0.06	0.3
^{89}Sr	1000 ml	42	1.2	0.3	0.9
^{90}Sr	1000 ml	33	1.2	0.1	0.5
Tritium	4 ml	30	9.0	150	500
	8 ml	23	9.5	70	300

*With these parameters, the procedures in this manual can obtain the corresponding minimum detection levels (MDL), assuming good chemical yield recovery. The calculations were made with data from replicate testing of these procedures. Variability in instrument background is a significant factor in the determination of these values. The levels reported above can be further reduced by the use of larger samples for analysis and better instrument shielding.
(Ref. 52, Appendix A, p. 41)

control programs.[a] The samples serve as independent checks on reagents, instruments or techniques, for training analysts, or for comparative analyses within the laboratory. There is no certification or other formal evaluative function resulting from their use. Further, no reports are prepared, and there is no requirement for use of EPA methods in these QC analyses.

The Quality Control samples are prepared as concentrates in sealed glass ampoules, and when diluted to volume with distilled or natural water, according to instructions, their concentrations of constituents range from minimum detectable levels to those found in heavily polluted streams.[b]

When an analytical procedure is adopted as a *Standard Method*, its acceptance becomes widespread throughout the nation and it is used by local and regional water and wastewater districts for routine public health surveillance. Consequently the reliability, reproducibility, and accuracy of the method are all important factors in its choice. One such procedure is the screening of waters for gross alpha and gross beta radioactivity (Ref. 5, p. 648). A study (Ref. 53) was conducted by the Environmental Protection Agency's Analytical Quality Control Service in which unknown samples were distributed to about 15 participating laboratories; the (gross alpha) activities were in the range of about 25 to 100 pCi/liter. Using the Standard Methods from the 12th Edition of the APHA compilation (Ref. 54), analyses were performed on each sample. The gross alpha measurements were found to agree quite well (the average activity found was 0.92 ± 0.10 of the known activity). To quote from Ref. 53:

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[a] Sample request cards are furnished by the appropriate AQC Regional Coordinator.

[b] For further information, contact:
John A. Winter, Chief
Quality Assurance Branch
Environmental Monitoring and Support Laboratory
Tel (513) 684-7326

> The results of the technical experiment show that this procedure for gross alpha...determination is acceptable as a standard method. As a screening technique, the procedure performed better than expected.

A brief discussion of the method for measuring gross α- and gross β-activity follows.

3.1 Measurement of Gross Alpha and Gross Beta Activity in Water

Measurements of gross alpha and gross beta levels in water are a mainstay of public-health monitoring systems. If the levels of these radiation parameters are shown to be low enough, it is usually unnecessary to identify and measure individual radionuclides using more complicated techniques.

Quoting in part from *Standard Methods, 14th Edition* (Ref. 5):

> By using the simpler technics for routine measurement of gross beta activity, the presence of contamination may be determined in a matter of minutes, whereas hours or even days may be required to conduct the radiochemical analyses necessary to identify the particular radionuclides that are present in the sample.
>
> Regular measurements of gross alpha and gross beta activity in water may be invaluable for early detection of radioactive contamination and indicate the need for supplemental data on the concentrations of the more hazardous radionuclides.

Method: Of the several methods used for analysis of gross alpha and gross beta activity in water, only the *Standard Method* (Ref. 5) from the APHA compilation will be considered here, because it is the one commonly used throughout the country for routine water monitoring. Reference 5 should be consulted for further details.

For counting gross alpha and gross beta an internal gas proportional counter is recommended: it has high-sensitivity, good geometrical efficiency, and reliability. The technique involves depositing a sample on a counting planchet, which is then inserted into the detector volume. The sample preparation is the difficult part. Because of the low range of alphas, only a very thin (≤ 3 mg/cm^2) sample can be used without the need for a significant self-absorption correction. The water sample is dried by oven evaporation just below the boiling temperature, or on a hot plate, then counted in the proportional counter. The main systematic error is from alpha-laden particles which might become airborne during the drying process. The recovery of gross alpha activity in this procedure is in the 85% to 90% range, with reproducibility (precision) of about ± 20%, at the 95% confidence level.

If separate determinations of suspended and dissolved matter are desired, a separation using a Gooch crucible or membrane filter is possible (Ref. 5).

In the presence of both alpha and beta activity, the alpha-beta separation can be accomplished by measuring the counting rate vs. voltage; a typical counter might respond as shown in Fig. 8a, where the first plateau is the α-plateau; the second, the sum of $(\alpha + \beta)$.

A calibration procedure involving uranium oxide (U_3O_8) is also described in Ref. 5 (p.643). The sensitivity of the method is excellent, with minimum detectable concentrations in the region of about 1 pCi/liter. Also, except for the possible volatile alpha-emitters (radon or thoron gas dissolved in water, for example), the method is both complete and without significant interference.

Alternative methods might employ either a thin-window proportional counter or a Geiger-Müller tube. Both have a lower counting efficiency, and the G-M tube has the added limitation of not separating alpha from beta activity.

A modification of the *Standard Method* for gross alpha and gross beta radiation has been adopted by the EPA/EMSL as the recommended interim method for the radiation screening of drinking water (Ref. 52).

The following excerpts from the EPA Environmental Monitoring Series (Ref. 57) ("Tentative Reference Method for the Measurement of Gross Alpha and Gross Beta Radioactivities in Environmental Waters") describe a calibration procedure and typical calculations.

3.11 Calibration

"Using standard solutions of cesium-137 (for beta radioactivity), americium-241 (for alpha activity) and tap water, prepare reference data for counting efficiency versus water solids per unit area of counting surface. Add known amounts of alpha and beta radioactivity to varying size aliquots of tap water. Evaporate the water aliquots, transfer the solids concentrate to tared counting dishes, dry, and count according to the procedure of Section 7.2.2. Correct the counting data for background activity and plot counting efficiency versus mg of solids per sq cm of counting dish area. Such a curve should be determined for each counting instrument for both alpha and beta and should cover the range of 0-10 mg per sq cm for beta and 0-5 mg per sq cm for alpha. Counting efficiencies for calculating gross alpha and gross beta radioactivities of environmental water sources are read from these curves.

3.12 Calculation and Reporting

"It is recommended that the gross alpha and gross beta radioactivities be determined and reported in pCi/liter. When counting beta radioactivity by gas flow proportional counting systems, alpha radioactivity present in the sample (or sample fraction) is counted also unless the particular instrument being used is designed and has been set for discriminating out the alpha pulses (higher energy). Without instrumental discrimination it is necessary to subtract the alpha activity (which had been counted at the alpha voltage plateau) from the beta plus alpha activity (counted at the beta voltage plateau). Determine alpha radioactivity by the following equation:

$$\text{Alpha (pCi/liter)} = \frac{\text{net cpm} \times c_1}{c_2 eV} \qquad (14)$$

where net cpm = gross alpha counts minus background counts at the alpha voltage plateau
c_1 = 1000 ml/liter
c_2 = 2.22 dpm/pCi
e = efficiency fraction, read from graph of efficiency versus mg of water solids per sq cm of counting dish area (alpha curve)
V = volume of the aliquot analyzed, in ml.

Determine beta radioactivity by the following equation:

$$\text{Beta (pCi/liter)} = \frac{\text{net cpm} \times c_1}{c_2 eV} - \text{alpha (pCi/liter)}^{*} \qquad (15)$$

where
c_1 = 1000 ml/liter
c_2 = 2.22 dpm/pCi
e = efficiency fraction, read from graph of efficiency versus mg of water solids per sq cm of counting dish area (beta graph)
net cpm = gross counts at the beta plateau voltage minus the background counts at the beta plateau voltage.

"Total water sample gross alpha and gross beta radioactivity is the sum of dissolved solids and suspended solids radioactivities if separated and analyzed separately."

Error associated with the results of the analysis should also be reported, and may be derived from the following considerations (Ref. 57).

3.13 Error and Statistical Calculations

"Because of the random nature of radioactivity disintegrations there is an error associated with any measured count of these disintegrations. The variability of any measurement is indicated by the standard deviation. The standard deviation in the counting rate is determined by the following equation:

$$\sigma(R) = \left(\frac{R_0}{t_1} + \frac{B}{t_2}\right)^{1/2} \qquad (16)$$

where
R_0 = gross count rate
t_1 = counting time for the gross count
B = background count rate
t_2 = counting time for the background count.

The counting error for a given sample expressed in pCi/liter and at the 95% confidence level is shown by:

$$E = \frac{c_1 \sigma(R) \times c_2}{c_3 eV}$$

where
c_1 = 1.96 = 95% confidence factor
c_2 = 1000 ml/liter
c_3 = 2.22 dpm/pCi
e = efficiency factor, cpm/dpm
V = volume of the aliquot analyzed, in ml

The standard deviation associated with the overall random uncertainty may be estimated by performing replicate analyses on a given sample, and is calculated from the following equation:

$$S_n = \left[\sum_{i=1}^{m} (n_i - \bar{n})^2/(m - 1)\right]^{1/2} \qquad (17)$$

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*The subtraction of alpha activity is necessary if the beta count is performed without instrumental discrimination for alpha counts.

where
n = activity (pCi/liter) of a given sample
$\bar{n}$ = mean activity (pCi/liter) of a series of analyses
m = the number of replicate analyses."

4. Calibration of Detectors

Absolute measurements of primary radioactive standards are carried out by means of coincidence and 4π counters. However, these instruments are not normally employed in routine radiochemical analyses (Ref. 24). Ordinarily detectors are calibrated using such prior-standardized radionuclides.

Standard solutions of some commonly encountered radionuclides may be obtained through the National Bureau of Standards (Ref. 43). Under specified conditions NBS will also accept samples for in-house standardization (Ref. 55). For additional information on sources see the following section (4.2 Calibration Sources) in this Chapter.

Usually radioactive decay rates are derived from readouts of counts and counting rates or from current-voltage data. Counting efficiency of the detector is determined by the measurement of sample count/rate and comparison with the rate obtained for the known standard nuclide. It is also sometimes possible to estimate counting efficiencies from geometric and other considerations - e.g., the extent of self-absorption as well as other radiation absorption prior to reaching the detector, and radiation scattered in and out of the system. Some of the relevant equations and calculations are given in Table 3 and in sections 3.11-3.13 just preceding.

Calibrations of counting instruments frequently make use of *efficiency vs. energy* plots. Since lower energy radiations are absorbed to a greater extent, counting efficiencies will increase with the energies of β-particles and weak x-rays. However, for γ-rays efficiency *decreases* with increasing energy because of reduced interactions of the higher energy photons within the detector.

In the construction of a counting efficiency curve, a set of radioactive standards of appropriate energy range is counted. It is important to consider the decay characteristics of each radionuclide in a sample in order to construct a generally applicable standard curve. This must compensate for interferences from other radiations, contributions from their partial decay, and counting losses by virtue of coincidences.

The counting efficiency selected for a particular analysis may actually be some average value for a known mixture of radionuclides in the sample, or it may be selected to reflect the value of some one nuclide - say, a particularly hazardous component. In any event, reported gross activity values should always include the counting efficiency value selected by the analyst.

4.1 Instrument Accuracy

The International Commission on Radiation Units (ICRU) in its Report No. 20 (Ref. 58) deals with the general question of instrument accuracy. Although primarily addressed to the calibration of instruments intended for health physics use, the remarks are generally applicable to the calibration of radiation detectors and are therefore quoted below:

> "The accuracy of a given instrument depends not only on the characteristics of the instrument but also on the care taken in its calibration and on the performance checks made during its use.
>
> "Calibrations may be carried out in several ways:
>
> (1) By national standard laboratories using calibration standards of the highest possible accuracy (ICRU, 1964; McNish, 1958).
>
> (2) By major government, academic, research or industrial laboratories using institutional standards established by careful comparison with a national standard (Clarke, et al., 1967).
>
> (3) By other groups using working standards (reference instruments) of lesser accuracy that are periodically calibrated by comparison with one of the above-mentioned national or institutional standards.

Only the last two will be discussed in this section.

"Calibration of instruments . . . involves the comparison of a given instrument with a reference instrument, or its irradiation in a field whose properties are either defined through use of a standard source, or which have been fully explored with a reference instrument. The calibration of the reference instrument may be determined by comparison with an institutional or national standard (ICRU, 1964).

"The object of calibrating an instrument intended for routine use is to ensure that its accuracy is adequate under the conditions in which it is used. This requires that assessment be made of its response not only to the type and energy of radiation for which the instrument was designed, but also to other radiations which may be present in practice and contribute to the instrument reading. It also requires that mechanical and electrical integrity, and effects such as saturation, reproducibility, pulse pile-up, scale non-linearity, and range-change errors be examined. Since manufacturers may not have adequate facilities for calibrating instruments, it is desirable to check new instruments after delivery. If the instrument has new design features, the check should be thorough, and include tests for the rejection of radiation which the instrument was not designed to measure, for pulse pile-up and for saturation. The effective center of the detector should be determined so that measurements of distance from the source of radiation can be made to this point; this is particularly important when the detector is situated within the instrument. This complete check need not be repeated for all instruments built to the same design. However, it is desirable to check every instrument for scale non-linearity and for range-change errors before putting it into service. The initial calibration may involve either a wide or narrow spectrum, or alternatively a complete energy response curve using a number of monochromatic sources may be required. The choice depends on the purpose for which the instrument is intended to be used and should test the claimed or advertised response characteristics.

"The frequency and scope of subsequent calibrations is governed by the rate at which components in the instrument age or become damaged. Unless there is evidence or experience to suggest that more frequent calibrations are desirable, yearly intervals are usually sufficient. Within these intervals simple constancy checks should be made to see that the instrument has not developed a calibration fault in any range. Such constancy checks, which are particularly important for instruments used only occasionally, can be made with jigs incorporating small sealed sources, or with leakage fields from a large installation (e.g., reactor, or accelerator) operating under steady conditions. The most satisfactory form of constancy check is one in which the sensitive element is irradiated by the type of radiation for which the instrument is designed. It should be carried out initially just after an instrument has been calibrated.

"The characteristic of an instrument which is most likely to change over a period of time is sensitivity. Some instruments provide an adjustment so that the reading can be brought back to the correct value when changes occur. In general, however, such adjustments should be made only at a calibration center having the standards needed to re-check the instrument over its whole absorbed dose or exposure range; changing sensitivity may not always be linear over the entire range of the instrument. Some instruments are fitted with a switch position for testing the battery and there may be a zero adjustment. It should be appreciated that the battery test may not check all the batteries. In these cases the batteries should be checked with an external voltmeter before calibration. The use of constancy checks is clearly important.....In general, the scope of yearly recalibrations should be the same as that of the initial calibration. However, the shape of the energy response curve is so unlikely to change with time for some instruments that they need be checked at only one or two energies throughout the whole response range after their initial calibration.

The purpose of a particular calibration procedure will determine the conditions under which it must be carried out. A distinction should be made between rigorously controlled tests in which the physical conditions approximate those appropriate to an absolute calibration and other tests in which the response of an instrument is evaluated under conditions similar to those in which it is to be used... Similarly, instruments intended for use as installed monitors could be calibrated under conditions approximating those which will obtain when they are installed. The *conditions of calibration should always be stated clearly in reports.* When instruments are purchased, it is important to obtain information about the nature and accuracy of any calibration that the manufacturer may have made. Such information should be a part of the specifications furnished by the manufacturer or distributor."

4.2 Calibration Sources

For calibration purposes, the analyst needs known standard sources. To satisfy this need, the U. S. National Bureau of Standards has for many years provided standard materials. These are briefly discussed in sections 4.21-4.25 which follow.

4.21 Alpha Standards

These samples "consist of a practically weightless deposit of the nuclide on a thin platinum foil 1.27 cm in diameter, which is cemented onto a monel disk 2.54 cm in diameter and 0.16 cm thick" (Ref. 43). Samples from NBS, available in the activity range from a few to a few thousand nanocuries, can be purchased for the isotopes ^{210}Po (E_α = 5.305 MeV), ^{238}Pu (E_α = 5.50, 5.46 MeV), and ^{241}Am (E_α = 5.49, 5.44 MeV). Table 18 is derived from the May 1976 listing of radioactivity standards (Ref. 43d).

4.22 Beta Particle and Gamma Ray Gaseous Standards

These are listed in Table 19 (also from Ref. 43d).

4.23 Standards in Other Forms

Standards are also provided by NBS in

TABLE 18. Alpha-Particle Standards (Ref. 43d)

Radionuclide	Approx. α-particle-emission rate into 2π geometry and/or approx. activity at time of calibration (month/year)		Overall uncertainty	SRN No.	Unit price	Notes
	(s^{-1})		(%)		($)	
Americium-241	2×10^3 to 5×10^4	2/70	± 1.0	4904-D	132	2,6
Gadolinium-148	50 to 2×10^4	1/73	1.7	4907	100	2
Plutonium-238	1×10^3 to 3×10^4	4/69	0.8	4906	166	2,7
Polonium-210	Made to order: 100α 200α		~ 1	4900 4901		1,29 1,29

TABLE 19. Beta-Particle and Gamma-Ray Gaseous Standards (Ref. 43d)

Radionuclide	Approx. activity, or emission rate, at time of calibration	(month/year)	Approx. volume	Overall uncertainty	SRM No.	Unit price	Notes
	(s^{-1})		(ml)	(%)		($)	
Argon-37	900	4/75	10	±1.8	4300-B	100	21
Argon-37	110	4/75	10	2.8	4301-B	100	21
Argon-39	3.3×10^4	7/75	10	1.5	4302	137	21
Argon-39					4303		25
Krypton-85	5×10^7 per mole	3/74	10	0.9	4935-C	108	4
Krypton-85	9×10^6 to 1.5×10^7	11/74	3	1.2	4235	108	4
Krypton-85	2×10^3 514-keVγs^{-1}	4/75	34.5	3.7	4308	106	29,17,22
Krypton-85 (ambient)					4309		25
Xenon-127					4310		23
Xenon-131m					4305		24
Xenon-133					4306		3, 24
Xenon-133					4307		5, 24

solution (α, β, γ - and e-capture) and *point source* form (γ-ray). Others include C-14 labeled oxalic acid for carbon dating, low energy photon standards, and a set of environmental standards. These are listed in Appendix 4.

4.24 X- and Gamma-Ray Calibration Sources

There are two common sources of photons for calibration purposes: x-ray tubes and radioactive gamma emitters. Since the response of many instruments is a strong function of energy, particularly at the lower energies, it is desirable to use as mono-energetic a source as possible.

In the case of radioactive sources, the intrinsically mono-energetic gamma energy can be degraded either by scattering or by absorption within the source itself, its container, or in air. Below a few tens of keV absorption is dominant, and care should be taken to account for it in the calibration procedure. This is particularly important because normally the detector should be far enough away that the finite instrument dimensions are not a major uncertainty in the measurement. Since knowing the effective 'center' of a detector to better than perhaps one third of the relevant dimension is often difficult, the detector usually has to be located several detector-diameters away from a source to reduce the $1/r^2$ uncertainties to ≤ 10%. Deviations from inverse-square fall-off of flux can be studied with a detector of much smaller dimensions than the distances involved.

Scattering is very important in the MeV range, because of the broad angular distribution of the Compton scattering cross-section. This makes it desirable to locate the calibration source as far as practical from large scattering surfaces such as walls.

Beams from x-ray tubes are useful mainly in the lower-energy region. The main problem here is the energy spectrum of the source, which usually has a broad spread even as it emerges from the tube. The low-energy tail on an x-ray spectrum can be greatly reduced in magnitude by the use of absorbers. To quote from Reference 58:

> "Care should be taken that secondary peaks are not introduced from the radiation produced by fluorescence of the filter material. For example, with a lead filter it may prove necessary to follow the lead with a tin filter to absorb the K radiation from the lead. Likewise, a copper filter may be required to absorb the K radiation from tin; an aluminum filter may be used to absorb the K radiation from copper. Normally high purity materials should be used as absorbers... For measurements of energy dependence below 100 keV, the K-fluorescence radiation of different elements can be used as an almost monoenergetic source of radiation. For most radiation protection applications the better energy definition obtained by this method is not required."

Table 20 (from Ref. 58) shows some common gamma-ray sources. Note that sources are available even in the low-energy region where x-ray tubes are also used. The last column shows the specific gamma-ray constant in units of Roentgen-meter^2/Curie-hour, which specifies numerically the exposure rate (R/hr) at 1 meter distance from 1 Curie of activity. However, these values may not be accurate enough for calibration purposes when scattering and absorption problems occur.

Two geometrical effects are particularly important: first, the angle of incidence of the radiation can affect the sensitivity of the detector, and the effect can be dependent on energy. Second, backscatter from large objects (e.g. a wall, human body, etc.) can significantly affect the response of an instrument. This can be checked by using an appropriately positioned phantom.

Since variations in humidity, temperature and pressure all affect instrument response, information relevant to the ambient conditions during calibration should always be included.

4.25 Sources for Calibration of Neutron Instruments[a]

In any neutron calibration measurement it is important to understand the source of neutrons: its energy spectrum, directionality, the presence or absence of equilibrium secondaries, and possible secondary sources present from scatter of the primary neutron flux.

One common calibration technique in the

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[a] The reader concerned primarily with the analysis of low level radiation in water may omit this section.

TABLE 20. Some gamma-ray calibration sources

Radionuclide	Effective Photon Energy (keV)	Half-life (Physical)	Specific Gamma-Ray Constant (R m^2/Ci hr)
Am-241	60	458 years	0.016
In-114m	192	50 days	0.043
Hg-203	279	47 days	0.12
Au-198	412	2.7 days	0.23
Cs-137	662	29.9 years	0.32
Co-60	1170,1330	5.23 years	1.30
Ra-226*	—	1608 years	0.825
Na-24	1370,2750	15 hours	1.83

*0.5 mm Pt filtration, decay products included.
From Ref. 58, as adapted in Ref. 1C.

fast-neutron region is the use of radioactive neutron sources from (α,n) reactions. Considerable research has been done on the determination of energy spectra from these sources, and a review paper by Hanson (Ref. 61) contains an excellent summary of information up to 1960. More recent work is summarized in ICRU Report No. 13 (Ref. 62). The most common sources are Po-Be, Ra-Be, Pu-Be, and Am-Be. Figure 9 from ICRU 13, shows the energy spectrum of neutrons from ^{241}Am-Be as measured by several groups. The purpose of the figure is to show how much difference exists among various investigators for Am-Be; this situation is also true for each of the other sources mentioned. The spectral uncertainties imply that absolute accuracies better than about ± 10% are probably not achievable with this method. One remaining problem is that the spectral studies have not generally extended below about 1 MeV, despite the fact that 20 to 30% of the neutrons in a typical source are in that low energy region (Ref. 62). The Am-Be source has one important advantage over the others, in that there is insignificant contamination from decay of daughters subsequent to Americium decay.

Fission is another common source of fast neutrons. Most data on energy spectra seem to fit the Maxwellian distribution function, where E is the fission neutron energy and E_n is an experimental parameter:

$$dN(E)/dE \sim E^{1/2} \exp(-E/E_n).$$

Experimental numbers for E_n are in the range 1.2 to 1.6 MeV for several fission nuclei, such as ^{233}U, ^{235}U, ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{252}Cf. A compilation of studies on fission spectra by Barnard et al. is summarized in ICRU No. 13 (Ref. 62).

The use of accelerators for production of nearly monoenergetic neutrons has been common; various reactions leading to a range of neutron energies are available. Some monoenergetic neutron-producing reactions are shown in Table 21.

TABLE 21. Monoenergetic neutron-producing reactions (Ref. 1c)

Reaction	Q-Value	Threshold Energy	Minimum Neutron Energy at 0°	Maximum Neutron Energy at Bombarding Energy		Maximum Bombarding Energy for Monoenergetic Neutrons
				2 MeV	3 MeV	
^{2}D(d,n)^{3}He	3.265	—	1.8[a]	5.24	6.26	—
^{3}T(p,n)^{3}He	−0.764	1.019	0.0639	1.20	2.21	—
^{3}T(d,n)^{4}He	17.6	—	12.4[a]	18.25	19.57	3.7
^{7}Li(p,n)^{7}Be	−1.647	1.882	0.0294	0.228	1.3	2.38
^{13}C(d,n)^{14}N	−0.281	0.328	0.00195	1.6	2.6	3.0
^{45}Sc(p,n)^{45}Ti	−2.79	2.908	0.00140	—	0.112	3.67
^{51}V(p,n)^{51}Cr	−1.562	1.565	0.00059	0.215[b]	—	2.36
^{65}Cu(p,n)^{65}Zn	−2.136	2.169	0.00051	0.214[c]	—	2.29

[a] Measured at 2.0 MeV, 150 degrees.
[b] At bombarding energy = 1.762 MeV.
[c] At bombarding energy = 2.368 MeV.

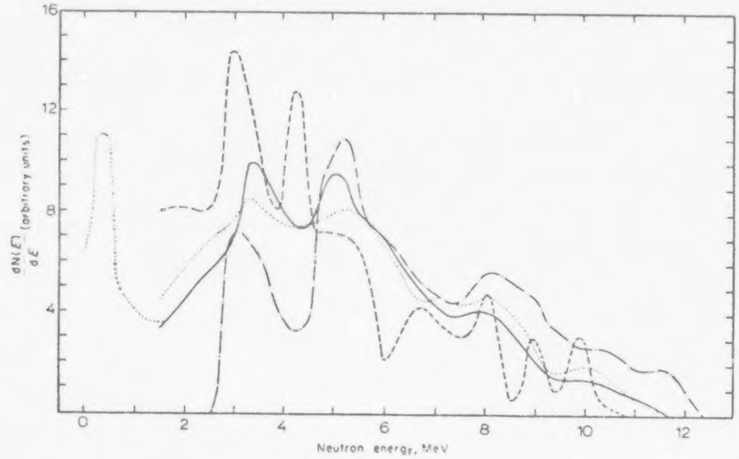

FIGURE 9. Energy distribution of ^{241}Am-Be neutrons according to different authors. The curves have been normalized to give the same total number of neutrons between energies 2.5 and 10.5 MeV: __________Geiger and Hargrove (1964), proton-recoil counter telescope and time of flight;----Greiss (1968), nuclear emulsions;·····Thompson and Taylor (1965), stilbene crystal with pulse-shape discrimination; —·—·—·— Salgir and Walker (1967), proton-recoil spectrometer (silicon detector). The dotted low energy peak has been drawn according to the suggestion of Geiger and Hargrove. (Ref.1c).

The directionality of the neutron source is sometimes difficult to determine, especially for thermal neutrons. The important problem here is the possible presence of scattered particles in addition to the primary flux. For accelerator-generated neutron beams the beam direction is well known, but beam halo is difficult to understand or reduce. For isotopic sources of small size, one can use a small detector to study departures from inverse-square fall-off of the flux. To minimize scattering problems, the physical layout for calibration must be carefully planned: for example, apparatus placed near a wall can be subject to large scattering corrections. A discussion of this, and of methods for measuring the possible scattering correction, can be found in ICRU Report No. 20 (Ref. 58).

In all calibrations, cross-comparison with standard instruments is extremely important. This is necessary to complement the understanding of the properties of the neutron source, because of possible unknown changes in the source.

As of this time, there does not exist a standard mechanism of calibrations for neutron instruments through any of the national standards bodies. Further, there are large regions in the neutron energy spectrum for which no well-understood neutron sources exist (Ref. 62): this is true in the region around 1 eV, and also near 2 keV. The available data are poor for many of the important cross-sections in the fast neutron region (e.g.,

$$^{31}\mathrm{P(n,p)}^{31}\mathrm{Si} \quad \text{and} \quad ^{115}\mathrm{In(n,n')}^{115}\mathrm{In}^{m}).$$

ICRU Report No. 13 contains a summary of basic research (primarily cross-section measurements) needed to make possible accurate neutron instrument calibrations.

4.3 Calibration: Procedure[a]

Calibration of a ratemeter type of instrument may be, but is not usually, a problem. The most important difficulty in calibrations is assuring a known geometry. For calibrating a dose-equivalent instrument, a known source can be used, but care must be exercised because of the finite thickness of the source itself: alphas of degraded energy, emerging from below the surface of the standard source, can influence the accuracy of the measurement. The source must be thin enough that none of the alphas are too degraded to register in the counter. The following calibration procedure for measuring mixed fission products with an internal proportional counter is derived from *Standard Methods* (Ref.5).

4.31 Calibration of Mixed Fission Products

To calibrate over-all counter efficiency a standard solution of C_s-137 with a composition similar to the unknown is prepared in aqueous solution. Increasing amounts of the solution are evaporated on tared pans, preparing samples with solids thicknesses varying from 1 to 10 mg/cm^2. Care must be duly exercised in the evaporation process to insure the uniform deposition of solids, and the samples are dried at 103-105°C, weighed and counted. The efficiency - e.g., the ratio of counts/minute (cpm) to the actual disintegrations/minute (dpm) for the series - is calculated, and a plot of efficiency versus sample thickness is made. This calibration curve is then used to convert cpm to dpm.

Where analyses of other radionuclides are involved, certified solutions of each are used and the procedure described above is repeated for each. It is essential to avoid the unequal distribution of solids, particularly in the range (0-3 mm thickness) for the calibration standards as well as the unknown samples. When inconsistent data are obtained they are, more often than not, traceable to this lack of uniformity in sample preparation.

The procedure described above is also applicable in calibration of the system for α-counting, except that a standard solution of a natural uranium salt is used to prepare the efficiency plot.

Coincidence Correction: Because G-M counters generally have resolving times of the order of 100-400 μseconds, data on high count-rate samples must be corrected for counting losses.

Other corrections: Observed counting rates must be corrected for factors affecting efficiency - namely, geometry, back-scatter and self-absorption (e.g. , sample absorption).

In addition variations in humidity, temperature and pressure all affect instrument response, and information relevant to these ambient conditions during calibration should always be included.

4.4 Calibration Service Centers

A detailed discussion of absolute national standards for instrument calibration is beyond the scope of this chapter. The National Bureau of Standards has for some years performed calibrations of x- and gamma-ray instruments against its own national standard (Ref. 43). However, the need for a larger number of calibration facilities has prompted the American

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[a] See also 4.24: X- and γ-Ray Calibration Sources for calibration precautions relevant to these sources.

Association of Physicists in Medicine (AAPM) to establish a certification system for Regional Calibration Laboratories. The primary motivation for these centers is for purposes of precise dosimetry in radiation therapy, but their use for radiation protection instrumentation will also be important. The centers, with secondary standards calibrated against the NBS national standard, perform routine calibrations of instruments for users. Information about the effort is available from the AAPM office (Ref. 60). The AAPM program is in progress with three certified regional centers: M. D. Anderson Hospital in Houston, Memorial Hospital in New York City and the Victoreen Company in Cleveland, Ohio. Certification of the latter was approved at the 1975 meeting of the AAPM (Aug. 3-7) according to Mark Presser, a physicist with Victoreen.

G. SUMMARY AND CONCLUSIONS

The determination of radionuclides in environmental water samples presents special problems, in that the radionuclide concentrations are generally low and difficult-to-remove interfering substances may be present as well. Nevertheless, it is usually possible to come up with some suitable modifications and/or combinations of known procedures from the voluminous analytical literature on radionuclides some of which has been quoted in this chapter. Procedures are available for all of the nuclides likely to be encountered in environmental waters and often the choice between primarily instrumental analysis and a wet-chemical separation reflects the preference of the analysts or the level of sophistication of instrumentation available in a given laboratory. Where large numbers of environmental samples are involved, the advantages of primarily instrumental methods are obvious.

There remains the need for improvement in the measurement of radionuclides at very low concentrations (Ref. 24) whether by increasing instrumental sensitivity or in the processing of extremely large quantities of water. In the latter instance the use of rapid evaporation techniques should be further explored where the loss of volatile activity is not a concern. A number of efficient concentrator designs are commercially available, usually depending on thin film evaporation. These will be included in a future chapter on SAMPLING in this volume.

The ideal instrument is one capable of measuring background levels with a high degree of accuracy; a number of laboratory techniques have this kind of sensitivity. However, laboratory instruments are often orders of magnitude more sensitive than their field monitoring counterparts (Ref. 1c).

There are two important considerations which determine the instrument sensitivity needed for measuring radionuclides in water:

a) the Maximum Permissible Concentrations (MPC), and b) the background level. Other requirements for the field instruments are: (1) rugged construction, insensitivity to changes in temperature and humidity; (2) some method of continuous recording of the data; at least a strip-recorder, or preferably a direct magnetic-tape record; (3) some method of calibration: perhaps a frequent, rapid check with a high energy source, and a less-frequent check in a controlled chamber of known nuclide concentration.

Accuracy and reproducibility of concentration procedures may be a problem. Accurate determinations of the fractional yield through a multi-stage sequence are often difficult.

There are a few technological developments on the horizon which will provide the increased sensitivity. The most important of these is the recent development of substantially better photomultiplier tubes. These tubes have higher quantum efficiency, lower noise, and generally superior operating characteristics. This will improve scintillation counting methods considerably.

The incorporation of integrated circuit electronics into G-M detector systems will also help to increase the ruggedness and reliability of these systems. Also, multi read-out systems are being developed, bypassing the strip-chart-recorder step entirely. These collect, record and analyze the data. Of particular interest vis a vis water analysis is the access to relatively large Ge(Li) detectors for X- and gamma-ray spectrometry as well as liquid scintillation counters used in the detection of the Cerenkov radiation produced by high energy betas.

For alphas, the salient physical features e.g., high energy, dense specific ionization and short range, make their detection relatively easy. Discrimination against other radiations is also easy. The difficulties with alpha detection unfortunately derive from these same physical properties. For example, it is often difficult to detect alpha activity if it is accidentally spilled on the floor, especially in cracks and near inaccessible corners. Also, alpha emitters contained deep within a soil sample (e.g., 50 micrometers or more below the surface) require chemical analysis prior to counting, as do alphas in water or urine. These problems have led to a variety of instrumental and chemical techniques.

For gross-alpha measurements, the standard method in water is sufficiently sensitive and well-understood to provide a satisfactory screening technique. The area most in need of further development is that of identification of individual nuclides. Alpha spectrometers with quite good resolution now exist, and their use makes possible the identification of many individual isotopic states *whenever good samples can be prepared*. Thus, proper sample preparation seems to be the crux of the problem.

Some of the sampling considerations relevant to radionuclide analysis have been summarized in section D.1 of this chapter (Sampling for Radionuclide Analysis). More extensive treatments of this subject may be found in References 4 and 5, and in the sampling section scheduled for later inclusion in this volume.

Present wet-chemical techniques, required to isolate alpha-emitting nuclides from background matrices such as soil, air filters, water, tissue and urine are laborious, liable to systematic error, and expensive. The use of tracers to follow chemical-yield fluctuations through a long chain of analytical steps is crucial. However, tracers are not universally available in convenient form, nor is there any way to guarantee their efficacy, especially when the alpha-emitters themselves are bound in multi-valent states in a variety of organic compounds (e.g., plutonium or uranium in soil).

While alpha *detection* is relatively well developed, quantitative measurements of *specific activity*, especially when isotopic identification is required, suffers important drawbacks because of cost, time, and sample-size considerations, except in cases where samples are easily prepared (Ref.1c).

With respect to low-radiation level environmental waters, the Environmental Monitoring Support Laboratory (EMSL) has published a series of *Tentative Reference Methods* (Refs. 57 and 70). These, along with the available screening methods for gross α and gross β-activity, provide a reasonably satisfactory analytical response capability at current contamination levels.

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APPENDIX 1

AGENCIES AND COMMITTEES CONCERNED WITH RADIATION CRITERIA STANDARDS

Name	Location	Function
International Commission on Radiological Protection (ICRP)	Clifton Ave., Sutton, Surrey United Kingdom	Establishes basic principles of radiation protection
International Atomic Energy Agency (IAEA)	Kaerntner Ring 11 A-1011 Vienna, Austria	Implements ICRP recommendations in international operations under UN auspices
International Commission on Radiological Units and Measurements (ICRU)	7910 Woodmont Ave. Bethesda, MD 20014	Recommends to ICRP: quantities and units of radiation; procedures and physical data needed to insure uniformity
National Committee on Radiation Protection and Measurement (NCRP)	Same as ICRP Tel.(202) 657-2652	Consists of a main committee and 20 subcommittees. Adapts ICRP recommendations to U.S. needs; is concerned only with Scientific/Technical aspects of radiation protection.
US/EPA, Division of Criteria and Standards, Office of Radiation Programs	Waterside Mall, East Tower 401 M Street, S.W. Washington, DC 20460 Tel.(202)755-4871	Sets non-occupational standards (MPC's); Monitors air and water. ERAMS programs.
Nuclear Regulations Commission (NRC)	Washington, DC 20555	Sets MPC's for their licensees
Energy Research and Development Administration (ERDA) Division of Safety, Standards and Compliance (Att. Edward J. Vallario, acting leader, standards group)	Washington, DC 20545 Tel.(301)353-5640 FTS 233-5640	Sets standards for ERDA facilities

APPENDIX 2

INTERIM PRIMARY DRINKING WATER REGULATIONS: RADIONUCLIDES

Title 40—Protection of Environment

CHAPTER 1—ENVIRONMENTAL PROTECTION AGENCY

[FRL 552-2]

PART 141—INTERIM PRIMARY DRINKING WATER REGULATIONS

Promulgation of Regulations on Radionuclides

On August 14, 1975, the Environmental Protection Agency (EPA) proposed national interim primary drinking water regulations for radioactivity pursuant to sections 1412, 1445, and 1450 of the Public Health Service Act ("the Act"), as amended by the Safe Drinking Water Act, Pub. L. 93–523, 40 FR 34324. Numerous written comments on the proposed regulations were received, and a public hearing was held in Washington on September 10, 1975.

The regulations for radioactivity are hereby promulgated in final form. A number of changes have been made in the proposed regulations in response to comments received. These changes represent efforts to clarify what are necessarily technical and complex provisions and to make monitoring requirements more realistic. The proposed maximum contaminant levels for radionuclides have been retained as proposed.

The comments received on the proposed regulations and EPA's response to those comments are discussed in detail in Appendix A. The promulgated radionuclides regulations and Appendix A should be read in the context of the national interim primary drinking water regulations as a whole. The regulations concerning microbiological, chemical and physical maximum contaminant levels, and related regulations dealing with public notification of violations and reports and record-keeping by public water systems, were promulgated on December 24, 1975, 40 FR 59566.

The balance of this preamble discusses briefly the five major issues highlighted in the preamble to the proposed radionuclides regulations, and lists in summary form the changes made in the proposed regulations.

The preamble of the proposed regulations listed five issues on which comment was particularly requested:

1. The number and location of the public water systems impacted by the proposed maximum contaminant levels for radionuclides.
2. The number and location of water supplies requiring radium analysis at the proposed 2 pCi/liter gross-alpha-particle-activity screening level.
3. The estimated preliminary assessments of the costs and technology for radium removal.
4. The validity and appropriateness of an aggregate dose method for setting maximum contaminant levels.
5. The acceptability of a maximum contaminant level for radium of 5 pCi/liter as opposed to a higher or lower level.

Public Water Systems Impacted: Little significant information was provided with respect to the number of community water systems that may exceed the proposed maximum contaminant levels. The State of Texas did report that 15 community water systems in that State would exceed the 5 pCi limit for radium: EPA estimated in the preamble to the proposed regulations that a total of approximately 500 of the Nation's community water systems would exceed the proposed radium limit. It is likely that relatively few community water systems currently exceed the proposed maximum contaminant levels for either gross alpha particle activity or man-made radioactivity. Those levels are intended as preventative limits rather than as corrective limits.

Public Water Systems Requiring Radium Analysis: The monitoring requirements for the radium maximum contaminant level provide for an initial screening measurement of gross alpha particle activity to determine if analysis for radium-226 is needed. EPA requested comment on the number and location of community water systems that would exceed the proposed screening level of 2 pCi/l. A number of comments were received on the possible impact of the proposed screening level. The principal concern expressed was that a 2 pCi/liter screening level was unnecessarily low and would force a large number of public water systems to conduct expensive radium analyses in cases where the radium limit was not being exceeded.

A number of commentors were under the impression that radium daughter products were in equilibrium with radium in drinking water so that their accompanying alpha particle activity would be an indication of radium. Monitoring data from many public water systems indicates that because of differences in solubility and geological processes, the alpha particle activity is frequently much lower than would be observed for an equilibrium mixture of radium and daughter products and sometimes may be no greater than that due to radium-226 alone.

EPA agrees that in many cases adequate protection can be obtained with a screening level higher than 2 pCi/liter provided that the precision of the measurement is great enough to insure that the gross alpha activity is unlikely to exceed 5 pCi/l. The regulations have been amended accordingly. The effect of this change is that a screening test, in lieu of radium analysis, is permitted for most systems having gross alpha particle activities as high as 4 pCi/l. However, as noted in the Statement of Basis and Purpose for the proposed radionuclide regulations, care should be taken in evaluating the results of the screening test because the alpha particle activity screen does not measure radium-228, a beta emitter. For this reason, EPA recommends that, in localities where radium-228 may be present in significant quantities, the State establish a screening level no greater than 2 pCi/liter.

Costs and Technology for Radium Removal: One comment on radium removal costs stated that the EPA cost estimates may be too high because new technologies for radium removal are being developed. Another comment stated that the EPA estimates appear "reasonable at this time," and a third that the estimates are "too general" in that system size was not considered.

As discussed in the Statement of Basis and Purpose for the proposed radionuclides regulations, costs for radium removal were found to be essentially independent of system size for systems treating less than three million gallons per day. Since there are no data indicating that the maximum contaminant level for radium is being exceeded in systems larger than this, the EPA cost estimates are valid.

Three commentors thought the cost projections for radium removal might be low because disposal of radium wastes was not considered. The Agency is presently conducting a research study to investigate disposal costs. Compared to industrial effluents containing radium, the amount of radium involved is quite small. The only available data indicate that a commercial waste disposal service for radioactive materials would be expected to cost about 50 cents annually per person served for radium disposal. However, costs will vary depending on locality and the disposal method used. It should also be noted that any radium disposal problems generated by the proposed regulations will not be unlike those already encountered by the many communities already removing radium as part of their water softening processing.

Other comments suggested consideration of occupational exposure to radium in water treatment plants. The Agency has made a limited examination of the levels of radiation in the vicinity of ion exchange units used to remove radium in operating water treatment plants. Exposure levels to operating personnel are measurable and occupational exposures could range up to 25–100 mrem/yr. These doses are well below the Federal occupational guides for radiation workers of 5000 mrem/yr. Appropriate Federal Radiation Guidance will be provided if future studies indicate the problem of occupational exposure to treatment plant personnel is serious.

One commentor questioned the efficiency of radium removal by ion exchange used in the cost analysis in Appendix V of the Statement of Basis and Purpose. That analysis shows that treatment cost is relatively independent of radium removal efficiency as long as removal exceeds 90 percent. Operating data from currently used municipal water treatment systems indicate that average radium removal efficiency throughout the exchange cycle ranges from 93 to 97 percent.

Aggregate Dose Level: As noted in the preamble to the proposed radionuclides regulations, 40 FR 34325, EPA considered but rejected the use of an aggregate dose level in establishing maximum contaminant levels. This approach would consider both the risk to individuals and the total risk to the population served, so that the maximum contaminant level would be inversely related, within limits, to the size of the exposed population group. Comments on the concept of aggregate dose levels overwhelmingly endorsed EPA's decision not to use that approach in the development of maximum levels under the Safe Drinking Water Act.

Maximum Contaminant Level for Radium: A number of States submitted comments on EPA's proposal to establish the maximum contaminant level for radium at 5 pCi/liter. One State suggested that a limit of 10 pCi/liter be established for small public water systems. This suggestion has not been accepted by EPA because the legislative history of the Safe Drinking Water Act indicates that, to the extent possible, all persons served by public water systems should be protected by the same maximum contaminant levels. A number of other States expressed concurrence in the 5 pCi/liter limit.

One commentor cited the results of a U.S. Public Health Service study that indicated that persons in communities with water having a concentration of 4.7 pCi/liter had a higher mortality incidence due to bone sarcoma than persons in communities with water having less than 1 pCi/liter. The commentor contended that the USPHS study did not show a significant difference in cancer risk at a 95 percent confidence level, and that in any event the number of excess cancers was significantly less than would be predicted on the basis of the NAS-BEIR Report.

EPA notes that the confidence level of the USPHS study was 92 percent which is not significantly different from a 95 percent criterion considering the overall precision of the USPHS study. Mortality estimates on which the 5 pCi/liter limit was based included all cancers, not just bone sarcoma. Moreover, the EPA estimates are for lifetime exposures, whereas most of the participants in the USPHS study were exposed for a substantially shorter period of time. Moreover, the incidence of cancer observed in the USPHS study is somewhat greater than would be predicted by the linear dose response model used by EPA, not less as suggested by the commentor. Given these facts it is EPA's view that the USPHS study supports its use of risk estimates from ingested radium as a valid measure of the impact of various control levels. EPA will, however, study new cancer incidence data as they become available to determine whether the 5 pCi/liter level provides appropriate protection.

Changes Made in the Proposed Regulations:

In response to comments received on the proposed regulations, a number of changes have been made. The comments and changes are discussed in some detail in Appendix A. The following list summarizes changes which have been made:

1. Section 141.2 has been revised to simplify the definitions of "gross alpha particle activity" and "gross beta particle activity." As proposed these definitions were confusing because they sought to make distinctions which were more properly set forth in §§ 141.15 and 141.16.

2. Section 141.15 has been changed to make clear that the maximum contaminant level for gross alpha particle activity does not apply to isotopes of uranium and radon.

3. Section 141.16 has been redrafted for clarity and provisions relating to the means of determining compliance have been moved to § 141.26. It should be noted that the average annual concentration of strontium-90 yielding 4 mrem per year to bone marrow is 8 pCi/l not 2 pCi/l as was stated in the Proposed Regulations. Accordingly, Table A in Section 141.16 has been corrected and the detection limit for strontium-90 listed in Table B, § 141.25 has been changed to 2pCi/l.

4. Section 141.25 has been revised to include newer analytical methods and to delete some obsolescent methods. The definition of detection limit has been changed to indicate clearly that it applies only to uncertainty in the precision of the measurement due to counting errors. Also, a new detection limit of 4 pCi/liter has been established for gross beta particle activity so that gross beta analysis may be substituted for strontium-89 and cesium-134 analyses in some cases. It should be noted that under § 141.27 the State, with the concurrence of the Administrator, may authorize the use of alternative analytical methods having the same precision and accuracy as those listed in §§ 141.25 and 141.26.

5. Section 141.26 has been redrafted for clarity and the alpha particle activity screening level has been redefined to provide a higher gross alpha screening limit as long as the precision of measurement insures that the gross alpha activity is unlikely to exceed 5 pCi/l. Also, the requirement for quarterly sampling has been revised to permit a yearly sample where a one-year record based on quarterly sampling has indicated the average annual gross alpha particle activity and radium-226 activity to be less than half the applicable maximum contaminant level. The period allowed for initial monitoring has been extended to three years rather than two years after the effective date of these regulations. Also, rather than require that subsequent monitoring be every three years for ground water and every five years for surface water, monitoring for both ground water and surface water will be required every four years.

6. Section 141.26 has been amended to provide that, when ordered by the State, a community water system will be required to participate in a watershed monitoring program for man-made radioactivity. EPA recommends that States require such programs in each principal watershed under their jurisdiction. In addition, the provision allowing the use of discharge data from nuclear facilities in lieu of special monitoring for man-made radioactivity has been amended to allow only the use of environmental surveillance data taken in conjunction with the State. Also in § 141.26 a screening level for gross beta particle activity has been established to reduce the cost of monitoring water systems affected by nuclear facilities.

If any screening levels for gross beta particle activity are exceeded, identification of specific radionuclides is mandatory prior to public notification and initiation of any enforcement action. In addition to the gross beta particle activity measurement, it may be necessary, as new energy technologies become available in the future, to monitor for specific man-made contaminants other than those currently identified. The Act provides that these regulations may be amended from time to time.

Effective Date

Section 1412(a)(3) of the Act provides that "The interim primary regulations first promulgated * * * shall take effect eighteen months after the date of their promulgation." The interim primary regulations first promulgated were those for microbiological, chemical and physical contaminants. They were promulgated on December 24, 1975, and will become effective June 24, 1977. Because it is desirable that all of the basic interim primary drinking water regulations take effect on the same date, and in view of the long lead time provided to public water systems for compliance with these radionuclide regulations, the radionuclide regulations also will become effective on June 24, 1977.

It is hereby certified that the economic and inflationary impacts of these regulations have been carefully evaluated in accordance with Executive Order 11821, and it has been determined that an Inflation Impact Statement is not required. (The estimated ten million dollar annual cost is less than the one-hundred million dollar annual cost cut-off established as the minimum for which an Inflation Impact Statement is required.)

For the reasons given above, Part 141, Chapter 40 of the Code of Federal Regulations is hereby amended as follows:

Russell Train,
Administrator.

June 25, 1976.

1. By revising § 141.2 to include the following new paragraphs (j) through (o):

§ 141.2 Definitions.

* * * * *

(j) "Dose equivalent" means the product of the absorbed dose from ionizing radiation and such factors as account for differences in biological effectiveness due to the type of radiation and its distribution in the body as specified by the International Commission on Radiological Units and Measurements (ICRU).

(k) "Rem" means the unit of dose equivalent from ionizing radiation to the total body or any internal organ or organ system. A "millirem (mrem)" is 1/1000 of a rem.

(l) "Picocurie (pCi)" means that quantity of radioactive material producing 2.22 nuclear transformations per minute.

(m) "Gross alpha particle activity" means the total radioactivity due to alpha particle emission as inferred from measurements on a dry sample.

(n) "Man-made beta particle and photon emitters" means all radionuclides emitting beta particles and/or photons listed in Maximum Permissible Body Burdens and Maximum Permissible Concentration of Radionuclides in Air or Water for Occupational Exposure, NBS Handbook 69, except the daughter products of thorium-232, uranium-235 and uranium-238.

(o) "Gross beta particle activity" means the total radioactivity due to beta particle emission as inferred from measurements on a dry sample.

2. By adding §§ 141.15, 141.16, 141.25 and 141.26 as follows:

§ 141.15 Maximum contaminant levels for radium-226, radium-228, and gross alpha particle radioactivity in community water systems.

The following are the maximum contaminant levels for radium-226, radium-228, and gross alpha particle radioactivity:

(a) Combined radium-226 and radium-228—5 pCi/1.

(b) Gross alpha particle activity (including radium-226 but excluding radon and uranium)—15 pCi/1.

§ 141.16 Maximum contaminant levels for beta particle and photon radioactivity from man-made radionuclides in community water systems.

(a) The average annual concentration of beta particle and photon radioactivity from man-made radionuclides in drinking water shall not produce an annual dose equivalent to the total body or any internal organ greater than 4 millirem/year.

(b) Except for the radionuclides listed in Table A, the concentration of man-made radionuclides causing 4 mrem total body or organ dose equivalents shall be calculated on the basis of a 2 liter per day drinking water intake using the 168 hour data listed in "*Maximum Permissible Body Burdens and Maximum Permissible Concentration of Radionuclides in Air or Water for Occupational Exposure,*" NBS Handbook 69 as amended August 1963, U.S. Department of Commerce. If two or more radionuclides are present, the sum of their annual dose equivalent to the total body or to any organ shall not exceed 4 millirem/year.

TABLE A.—*Average annual concentrations assumed to produce a total body or organ dose of 4 mrem/yr*

Radionuclide	Critical organ	pCi per liter
Tritium	Total body	20,000
Strontium-90	Bone marrow	8

§ 141.25 Analytical Methods for Radioactivity.

(a) The methods specified in *Interim Radiochemical Methodology for Drinking Water*, Environmental Monitoring and Support Laboratory, EPA-600/4-75-008, USEPA, Cincinnati, Ohio 45268, or those listed below, are to be used to determine compliance with §§ 141.15 and 141.16 (radioactivity) except in cases where alternative methods have been approved in accordance with § 141.27.

(1) Gross Alpha and Beta—Method 302 "Gross Alpha and Beta Radioactivity in Water" *Standard Methods for the Examination of Water and Wastewater*, 13th Edition, American Public Health Association, New York, N.Y., 1971.

(2) Total Radium—Method 304 "Radium in Water by Precipitation" Ibid.

(3) Radium-226—Method 305 "Radium-226 by Radon in Water" Ibid.

(4) Strontium-89,90 — Method 303 "Total Strontium and Strontium-90 in Water" Ibid.

(5) Tritium—Method 306 "Tritium in Water" Ibid.

(6) Cesium-134 — ASTM D-2459 "Gamma Spectrometry in Water," *1975 Annual Book of ASTM Standards, Water and Atmospheric Analysis*, Part 31, American Society for Testing and Materials, Philadelphia, PA. (1975).

(7) Uranium—ASTM D-2907 "Microquantities of Uranium in Water by Fluorometry," Ibid.

(b) When the identification and measurement of radionuclides other than those listed in paragraph (a) is required, the following references are to be used, except in cases where alternative methods have been approved in accordance with § 141.27.

(1) *Procedures for Radiochemical Analysis of Nuclear Reactor Aqueous Solutions*, H. L. Krieger and S. Gold, EPA-R4-73-014. USEPA, Cincinnati, Ohio, May 1973.

(2) *HASL Procedure Manual*, Edited by John H. Harley. HASL 300, ERDA Health and Safety Laboratory, New York, N.Y., 1973.

(c) For the purpose of monitoring radioactivity concentrations in drinking water, the required sensitivity of the radioanalysis is defined in terms of a detection limit. The detection limit shall be that concentration which can be counted with a precision of plus or minus 100 percent at the 95 percent confidence level (1.96σ where σ is the standard deviation of the net counting rate of the sample).

(1) To determine compliance with § 141.15 (a) the detection limit shall not exceed 1 pCi/l. To determine compliance with § 141.15(b) the detection limit shall not exceed 3 pCi/l.

(2) To determine compliance with § 141.16 the detection limits shall not exceed the concentrations listed in Table B.

TABLE B.—DETECTION LIMITS FOR MAN-MADE BETA PARTICLE AND PHOTON EMITTERS

Radionuclide	*Detection limit*
Tritium	1,000 pCi/l.
Strontium-89	10 pCi/l.
Strontium-90	2 pCi/l.
Iodine-131	1 pCi/l.
Cesium-134	10 pCi/l.
Gross beta	4 pCi/l.
Other radionuclides	1/10 of the applicable limit.

(d) To judge compliance with the maximum contaminant levels listed in sections 141.15 and 141.16, averages of data shall be used and shall be rounded to the same number of significant figures as the maximum contaminant level for the substance in question.

§ 141.26 Monitoring Frequency for Radioactivity in Community Water Systems.

(a) Monitoring requirements for gross alpha particle activity, radium-226 and radium-228.

(1) Initial sampling to determine compliance with § 141.15 shall begin within two years of the effective date of these regulations and the analysis shall be completed within three years of the effective date of these regulations. Compliance shall be based on the analysis of an annual composite of four consecutive quarterly samples or the average of the analyses of four samples obtained at quarterly intervals.

(i) A gross alpha particle activity measurement may be substituted for the required radium-226 and radium-228 analysis *Provided*, That the measured gross alpha particle activity does not exceed 5 pCi/1 at a confidence level of 95 percent (1.65σ where σ is the standard deviation of the net counting rate of the sample). In localities where radium-228 may be present in drinking water, it is recommended that the State require radium-226 and/or radium-228 analyses when the gross alpha particle activity exceeds 2 pCi/1.

(ii) When the gross alpha particle activity exceeds 5 pCi/1, the same or an equivalent sample shall be analyzed for radium-226. If the concentration of radium-226 exceeds 3 pCi/1 the same or an equivalent sample shall be analyzed for radium-228.

(2) For the initial analysis required by paragraph (a)(1), data acquired within one year prior to the effective date of this part may be substituted at the discretion of the State.

(3) Suppliers of water shall monitor at least once every four years following the procedure required by paragraph (a)(1). At the discretion of the State, when an annual record taken in conformance with paragraph (a)(1) has established that the average annual concentration is less than half the maximum contaminant levels established by § 141.15, analysis of a single sample may be substituted for the quarterly sampling procedure required by paragraph (a)(1).

(i) More frequent monitoring shall be conducted when ordered by the State in the vicinity of mining or other operations which may contribute alpha particle radioactivity to either surface or ground water sources of drinking water.

(ii) A supplier of water shall monitor in conformance with paragraph (a)(1) within one year of the introduction of a new water source for a community water system. More frequent monitoring shall be conducted when ordered by the State in the event of possible contamination or when changes in the distribution system or treatment processing occur which may increase the concentration of radioactivity in finished water.

(iii) A community water system using two or more sources having different concentrations of radioactivity shall monitor source water, in addition to water from a free-flowing tap, when ordered by the State.

(iv) Monitoring for compliance with § 141.15 after the initial period need not include radium-228 *except when* required by the State, *Provided*, That the average annual concentration of radium-228 has been assayed at least once using the quarterly sampling procedure required by paragraph (a)(1).

(v) Suppliers of water shall conduct annual monitoring of any community water system in which the radium-226 concentration exceeds 3 pCi/1, when ordered by the State.

(4) If the average annual maximum contaminant level for gross alpha particle activity or total radium as set forth in § 141.15 is exceeded, the supplier of a community water system shall give notice to the State pursuant to § 141.31 and notify the public as required by § 141.32. Monitoring at quarterly intervals shall be continued until the annual average concentration no longer exceeds the maximum contaminant level or until a monitoring schedule as a condition to a variance, exemption or enforcement action shall become effective.

(b) Monitoring requirements for manmade radioactivity in community water systems.

(1) Within two years of the effective date of this part, systems using surface water sources and serving more than 100,000 persons and such other community water systems as are designated by the State shall be monitored for compliance with § 141.16 by analysis of a composite of four consecutive quarterly samples or analysis of four quarterly samples. Compliance with § 141.16 may be assumed without further analysis if the average annual concentration of gross beta particle activity is less than 50 pCi/1 and if the average annual concentrations of tritium and strontium-90 are less than those listed in Table A, *Provided*, That if both radionuclides are present the sum of their annual dose equivalents to bone marrow shall not exceed 4 millirem/year.

(i) If the gross beta particle activity exceeds 50 pCi/1, an analysis of the sample must be performed to identify the major radioactive constituents present and the appropriate organ and total body doses shall be calculated to determine compliance with § 141.16.

(ii) Suppliers of water shall conduct additional monitoring, as ordered by the State, to determine the concentration of man-made radioactivity in principal watersheds designated by the State.

(iii) At the discretion of the State, suppliers of water utilizing only ground waters may be required to monitor for man-made radioactivity.

(2) For the initial analysis required by paragraph (b)(1) data acquired within one year prior to the effective date of this part may be substituted at the discretion of the State.

(3) After the initial analysis required by paragraph (b)(1) suppliers of water shall monitor at least every four years following the procedure given in paragraph (b)(1).

(4) Within two years of the effective date of these regulations the supplier of any community water system designated by the State as utilizing waters contaminated by effluents from nuclear facilities shall initiate quarterly monitoring for gross beta particle and iodine-131 radioactivity and annual monitoring for strontium-90 and tritium.

(i) Quarterly monitoring for gross beta particle activity shall be based on the analysis of monthly samples or the analysis of a composite of three monthly samples. The former is recommended. If the gross beta particle activity in a sample exceeds 15 pCi/1, the same or an equivalent sample shall be analyzed for strontium-89 and cesium-134. If the gross beta particle activity exceeds 50 pCi/1, an analysis of the sample must be performed to identify the major radioactive constituents present and the appropriate organ and total body doses shall be calculated to determine compliance with § 141.16.

(ii) For iodine-131, a composite of five consecutive daily samples shall be analyzed once each quarter. As ordered by the State, more frequent monitoring shall be conducted when iodine-131 is identified in the finished water.

(iii) Annual monitoring for strontium-90 and tritium shall be conducted by means of the analysis of a composite of four consecutive quarterly samples or analysis of four quarterly samples. The latter procedure is recommended.

(iv) The State may allow the substitution of environmental surveillance data taken in conjunction with a nuclear facility for direct monitoring of manmade radioactivity by the supplier of water where the State determines such data is applicable to a particular community water system.

(5) If the average annual maximum contaminant level for man-made radioactivity set forth in § 141.16 is exceeded, the operator of a community water system shall give notice to the State pursuant to § 141.31 and to the public as required by § 141.32. Monitoring at monthly intervals shall be continued until the concentration no longer exceeds the maximum contaminant level or until a monitoring schedule as a condition to a variance, exemption or enforcement action shall become effective.

APPENDIX A

RESPONSE TO PUBLIC COMMENTS

Proposed National Interim Primary Drinking Water Regulations for radionuclides, 40 FR 34324, were published for comment on August 14, 1975. Written comments on the proposed regulations were received, and a public hearing on the proposal was held in Washington on September 10, 1975. As a result of review of the written comments and of testimony at the public hearing, as well as further consideration of the available data by EPA, a number of changes have been made in the proposed regulations. The principal changes are summarized in the Preamble to the final regulations. The purpose of this Appendix is to discuss the comments received on various aspects of the proposed regulations, and to explain EPA's response to those comments.

Part I of the Appendix deals with comments on specific provisions of the proposed regulations, in numerical order. Part II concerns more general comments received by EPA. Responses to the five specific issues on which comments were solicited in the August 14 proposal are reviewed and discussed in the preamble to the promulgated regulations. Part III is the Agency's policy Statement of March 3, 1975, on the Relationship between radiation dose and effect.

PART I

Comments on Specific Provisions of the Proposed Regulations § 141.2—Definitions

A number of commentors stated that the definitions given in § 141.2 for gross beta particle and gross alpha particle activity were confusing because they excluded certain radionuclides. These definitions have been redrafted to omit the exclusions, which are more properly dealt with in the basic regulations.

§ 141.15—MAXIMUM CONTAMINANT LEVELS OF RADIUM-226, RADIUM-228, AND GROSS ALPHA PARTICLE RADIOACTIVITY

Several comments suggested that the maximum contaminant level for gross alpha particle activity should state clearly that this limit does not apply to isotopes of uranium and radon. This was the intention of the proposed regulations, and § 141.15 has been redrafted accordingly. Some commentors requested clarification of the impact of the exclusion of uranium and radon on monitoring procedures and compliance. It is true that the sample preparation techniques specified in § 141.25 preclude the measurement of the gaseous radionuclides radon-220 and radon-222. Their daughter products, however, will be retained in the sample as intended by these regulations. As noted in the Statement of Basis and Purpose, one of the main intentions of the maximum contaminant level for gross alpha particle activity is to limit the concentration of long half-life radium daughters. In cases where gross alpha particle activity exceeds 15 pCi per liter, analysis of the water for its uranium content by chemical or other means will be needed to determine compliance. Except in ground water impacted by uranium-bearing ores, such analyses will rarely be necessary.

Two commentors mentioned that no rationale for the gross alpha particle maximum contaminant limit of 15 pCi/1 was given in the preamble to the proposed regulations. The rationale for this limit is, however, discussed in the Statement of Basis and Purpose. It is based on a consideration of the radiotoxicity of other alpha particle emitting contaminants relative to radium. The 15 pCi/1 gross alpha particle limit, which includes radium-226 (but not uranium or radon), is based on the conservative assumption that if the radium concentration is 5 pCi/1 and the balance of the alpha particle activity is due to the next most radiotoxic alpha particle emitting chain starting with lead-210, the dose to bone will not be unduly increased. Though less precise than setting maximum contaminant levels for lead-210 specifically, the establishment of a limit on gross alpha particle activity is more in keeping with the current capability of State laboratories while providing significant public health protection. Reasons for omitting uranium and radon from the limit for gross alpha particle activity are given in the Statement of Basis and Purpose.

§141.16—MAXIMUM CONTAMINANT LEVELS OF BETA PARTICLE AND PHOTON RADIOACTIVITY FROM MAN-MADE RADIONUCLIDES

Several commentors had difficulty interpreting this section. It has been redrafted and that portion of the proposed maximum contaminant level for man-made radioactivity dealing with compliance has been moved to § 141.26 for purposes of clarity.

One commentor questioned the basis of the selection of the proposed 4 millirem annual limit. As stated in the preamble to the proposed regulations, the four millirem per year limit for man-made radioactivity was chosen on the basis of avoiding undesirable future contamination of public water supplies as a result of controllable human activities. Current levels of radioactivity in public water systems are below the proposed limit. Appropriate data on this point is provided in the Statement of Basis and Purpose.

Reference was made by one commentor to the Nuclear Regulatory Commission design criteria for light water reactors which limits the thyroid dose from a single nuclear reactor due to the liquid pathway to ten millirem per year. The commentor suggested that this number is in conflict with the proposed maximum contaminant level for man-made radioactivity. However, because the two levels are computed on different bases, iodine-131 concentrations meeting NRC design criteria would also meet maximum contaminant limits. Therefore, there is no conflict between these regulations and NRC design criteria. It should be noted, however, that the NRC limits are design criteria, not operational limits, and apply to only a single nuclear reactor. The EPA maximum contaminant limits have a completely different application. They apply to the finished waters served by a community water system which may use source waters contaminated by several reactors or other nuclear facilities.

Another commentor stated that the strontium-90 maximum contaminant level would produce a bone cancer dose of 4 millirem per year only after several decades of intake. That is correct—all of the maximum contaminant levels are based on an assumed lifetime ingestion at the concentration limits.

A few commentors stated that because in some localities the dose from strontium-90 in milk exceeds 4 mrem per year, the maximum contaminant level for strontium-90 in drinking water should be eliminated or made greater. The Administrator does not agree that the radioactive contamination of milk and milk products, which may occur in some localities, is a proper basis for relaxing maximum contaminant levels for drinking water. The maximum contaminant level for strontium-90 is not exceeded in community water systems at present nor is it likely to be exceeded in the foreseeable future. To permit unnecessary contamination of public water systems because of other environmental pathways impacting on man would be inappropriate.

A few commentors suggested that 2 liters per day was not an appropriate ingestion rate assumption for drinking water. The Administrator notes that a 2 liter per day intake is assumed for establishing maximum contaminant levels for all contaminants, not just radioactivity, and that this question has been discussed at length in the preamble and Appendix A to the National Interim Primary Drinking Water Regulations, 40 FR 59575.

A few commentors asked why potassium-40 was not considered as part of the maximum contaminant level for beta particle radioactivity. The amount of potassium in the body is controlled homeostatically and is not proportional to water intake levels. Without the exception for potassium-40, some communities might be required to perform more analytical examination than necessary if waters exceeded the gross beta activity screening level. If the increased beta activity is due to potassium-40, there is no increased risk to users of the public water systems and therefore such tests are unnecessary.

§ 141.25—ANALYTICAL METHODS FOR RADIOACTIVITY

Several commentors noted that the Proposed Regulations on analytical methods did not allow for the substitution of equivalent alternative techniques. EPA agrees that this is an important consideration and § 141.27 has been added to the regulations to allow substitution of equivalent analytical methods with the approval of the State and the Administrator. Two commentors believed that no analytical methods should be specified as part of the regulations, 40 FR 34324. The Administrator believes, however, that defined analytical methods must be a part of the regulations so that compliance procedures are uniform and subject to verification.

Many commentors believed that alternative analytical methods were preferable to those listed in the proposed regulations and several made specific suggestions. EPA recognizes that some of the proposed analytical methods were obsolescent and for this reason a new handbook, *Interim Radiochemical Methodology for Drinking Water*, has been prepared by the Agency. § 141.25 has been revised to include these new methods and to delete some of the analytical methods proposed earlier. However, some Standard Methods have been retained because they are equivalent to the newer procedures and are currently being used by State laboratories.

Several comments concerned the need for laboratory certification and quality assurance. EPA will seek to certify at least one State laboratory in each State. The State may in turn certify additional laboratories. Pursuant to § 141.28, only monitoring results from laboratories approved or certified by the entity with primary enforcement responsibility will be acceptable.

Several comments were received concerning application of the defined detection limits. The detection limit requirements have been changed to indicate clearly that the limit applies only to uncertainty in the precision of the measurement due to counting errors. Other sources of imprecision and the overall accuracy of the determination are not a part of the detection limits given in this section but rather their control is to be implemented by means of the quality assurance program mentioned previously.

A few commentors believed that the proposed detection limit for gross alpha particle activity was too low. Because systems using very hard water may be unable to detect alpha particle activity at the 1 pCi/l concentration, the detection limit for compliance with the gross alpha particle activity limit, § 141.15(b) has been increased to 3 pCi/l. This higher detection limit is not acceptable for gross alpha particle measurements substituted for radium analysis under § 141.26(a)(1)(i). If water hardness precludes use of this screening test, a radium analysis must be made to demonstrate compliance with § 141.15(a) of these regulations.

Most commentors believed the detection limits for man-made radioactivity were low but practicable in laboratories where modern testing facilities are available.

§ 141.26—MONITORING REQUIREMENTS FOR ALPHA PARTICLE AND RADIUM ACTIVITY

The major comments on § 141.26(a) were that the requirements were not clearly written and that the alpha particle activity screening test for a mandatory radium-226 measurement was too low thus necessitating unnecessary expense without increasing protection to the public health. Paragraph (a) has been redrafted to clarify the intent of these regulations; and, as discussed in the preamble to these regulations, the gross alpha particle screening level has been increased.

Some commentors objected to the requirement that quartely monitoring be continued when maximum contaminant levels are exceeded and others asked why quarterly sampling is needed. The reason why quarterly monitoring may provide additional public health protection where maximum contaminant levels are exceeded is discussed in the Statement of Basis and Purpose. The Agency agrees that quarterly sampling may be unnecessary in some cases and has amended the regulations to allow a single yearly sample where a one year historical record based on quarterly sampling shows the average annual gross alpha particle activity and the radium-226 activity to be less than one-half the applicable maximum contaminant levels.

Comments were divided on sampling frequency. Citizen groups tended to want more frequent monitoring and the States less frequent monitoring. Of particular public interest was the possible contamination of ground and surface water by mining operations. The revised regulations encourage the State to require more frequent monitoring for natural radioactivity in situations where mining or other operations may impact on water quality, when new sources of supply water are utilized or when water treatment processing is changed by the supplier of a community water system.

Several commentors requested an extension of the initial two-year period proposed for mandatory compliance. EPA is aware that these regulations call for a more expanded monitoring effort than is presently being carried out by most States. The regulations have been revised to require that initial monitoring begin within two years and that analysis be completed within three years of the effective date. In addition, the Agency has reconsidered, as suggested by several commentors, the proposed requirement that ground water be monitored every three years and surface water every five years and believes monitoring every four years for each is appropriate. The regulation has been so amended.

A few States requested that the initial monitoring of any community water system for radioactivity be at the discretion of the State and that the frequency of monitoring be determined by each State on a case by case basis. This is essentially the system now used. Congress has mandated improved control of drinking water quality, and these regulations seek to carry out that mandate.

Two commentors objected to the Agency's use of a gross alpha screening test to determine the need for radium-228 measurements because such a test is not applicable to radium-228, a beta emitter. Since radium-226 and radium-228 are not part of the same decay series, one of the commentors believed an evaluation which measures only gross alpha particle activity was inappropriate. It is true that radium-226 and radium-228 are in different decay series. However, the available monitoring data indicate that there is no record of radium-228 occurring in community water systems unless it is accompanied by radium-226. As pointed out in the Statement of Basis and Purpose, the radium-226 concentration in public water supply systems is almost always greater than the radium-228 concentration. Therefore, a screening test based on gross alpha particle activity is valuable for determining when further testing for specific radionuclides is necessary. However, States are encouraged to require specific analyses for both radium-226 and radium-228 where radium-228 may be present.

Several commentors raised questions concerning the points at which samples are to be taken and the procedure to be followed where multiple, or alternate, sources are utilized. As indicated in both the Statement of Basis and Purpose, and § 141.2(e) of the Interim Primary Drinking Water Regulations, sampling is to be done at the "free-flowing outlet of the ultimate user." Where multiple sources are employed, the samples should represent an unbiased estimate of the maximum concentration of radionuclides ingested by persons served by the system.

The Administrator recognizes that in some communities several wells are used at different periods throughout the year to supply drinking water and that because of different concentrations of radioactivity in these wells the concentration in finished water may fluctuate considerably. It is recommended that in such cases the States require augmented sampling programs which include monitoring of source waters. In the revised regulations the State has been given authority to order such monitoring.

§ 141.26(b)—MONITORING REQUIREMENTS FOR MAN-MADE RADIOACTIVITY

There were two types of objection to the proposal that mandatory monitoring for man-made radioactivity be confined to systems serving more than 100,000 persons and systems impacted by nuclear facilities. Some commentors felt that all systems, including those utilizing ground water, should be monitored. Others believed that monitoring only systems serving large communities would not adequately reflect the situation in their States.

EPA believes that because of cost and the size and number of laboratories available now to do the radiochemical analysis required for man-made radioactivity, monitoring efforts are better directed at those systems which are most likely to be contaminated by man-made radioactivity. However, the State should require monitoring for man-made radioactivity in each principal watershed under its jurisdiction as necessary to determine the extent of radioactivity in surface waters. The regulations have been so amended.

Commentors representing consumers, States, and industry objected to the provision that discharge data from nuclear facilities could be used in lieu of monitoring for man-made radioactivity. This provision has been redrafted to reflect more adequately the intention of this provision. Suppliers may use data obtained through an environmental surveillance program conducted by a nuclear facility in conjunction with the State to show compliance with these regulations. In many cases these monitoring programs will include more complete and frequent analyses of radioactivity in source and finished waters than would normally be available through State efforts alone.

A few comments stated that the proposed monitoring for specific radionuclides in the vicinity of nuclear facilities would often be unnecessary and that if such tests could be preceded by a screening test for gross beta particle activity, monitoring costs would be reduced. EPA agrees with these comments as they apply to the required quarterly monitoring for strontium-89 and cesium-134. The regulations concerning monitoring in the vicinity of nuclear facilities have been amended to establish a screening level for gross beta particle activity of 15 pCi/l. Only if this concentration is exceeded is measurement of strontium-89 and cesium-134 required. Tritium and iodine-131 are not measured by a test for gross beta particle activity and the requirement for analyses for these radionuclides is retained.

Some commentors pointed out that monitoring for iodine-131 as proposed was unrealistic since a single "grab" sample per quarter might not detect intermittent discharges from nuclear facilities. Other commentors stated that the decay of iodine-131 would render any measurements meaningless. While there is merit in both arguments, continuous monitoring for iodine-131 is impractical in many cases because of cost considerations. However, monitoring for iodine-131 will be more meaningful if, each quarter, a sample based on five successive daily composites is measured, as required in the revised regulations. This measurement should be made as soon as possible after collection and appropriate decay corrections applied as outlined in *Interim Radiochemical Methodology for Drinking Water*, referenced in §141.25(a).

Several commentors requested supplemental information on the storage and analysis of composited quarterly samples. Additional comments questioned the feasibility of compositing quarterly samples for iodine-131 monitoring and the need to correct for decay between the time samples are collected and measured. The required treatment for the preservation of composited samples is discussed in both the Statement of Basis and Purpose and the reference cited above. In the case of iodine-131, hydrochloric rather than nitric acid should be used for acidification and sodium bisulfite should be added to the sample.

A few commentors requested that cesium-137 be included with cesium-134 in the monitoring program for man-made radioactivity. The Administrator believes, in the interest of cost, that only one cesium isotope measurement should be mandatory. Measurement of cesium-134, which provides more information on changes in environmental levels than cesium-137 monitoring, is preferable. However, States may include cesium-137 monitoring if they desire to do so. In many cases costs will not be affected significantly. When beta activity exceeds 50 pCi/l, identification of major radioactive constituents is required. The extent of such analysis should be based on the States' determination of what radionuclides are likely to be present in the water and the maximum dose that could be delivered by unidentified components.

A few commentors requested additional guidance on calculating the concentration of radioactivity yielding 4 mrem per year, based on NBS Handbook 69, as required by these Regulations. The Administrator anticipated this problem and the Agency is publishing a revised Statement of Basis and Purpose which includes a table giving the concentration that is calculated to result in a dose equivalent rate of 4 mrem per year from all radionuclides of interest. The revised Statement also contains other pertinent information needed to facilitate compliance with these regulations.

PART II

General Comments

Monitoring and treatment costs

Many comments were received on the Agency's estimate of monitoring costs under these proposed regulations. One State supplied cost estimates which were lower than analytical costs estimated in the preamble. Another State thought that cost estimates in the preamble "were about right." However, all other commentors thought that the cost estimates made by EPA were too low. There are several reasons for this difference of opinion. In some cases commentors provided an analysis of their estimated cost for compliance based on sampling frequencies in excess of those required by the proposed regulations and the use of additional test analyses not required by the regulations. Another source of difficulty was that, as stated in the preamble, the cost per sample did not include collection and shipping charges. One State estimated this cost as high as $15.00 per sample. No other examples were provided, however. This Agency's cost for obtaining one gallon water samples for its Eastern Environmental Radiation Facility in Alabama is, exclusive of labor costs: container cost, $.62; shipping empty, $1.00; return full container, $6.00. Since analyses for gross alpha particle activity and radium require less volume, States costs for most community water supplies should be lower.

A major source of disparity between Agency and commentor cost estimates was that the EPA estimates did not include capital equipment costs. This is particularly important for States having essentially no ongoing program for measuring radioactivity in water. In such cases the cost estimates will be exceeded if a new laboratory program must be established. In most cases, however, State laboratories are available with at least some equipment for initiating the required monitoring program.

Two states objected to the monitoring costs for natural radioactivity on the basis that they were not cost effective for small public water systems. They contended that monitoring should be restricted to large community water supplies. The Administrator believes that the requirements of the Safe Drinking Water Act are such that the quality of water served by community water supply systems should be independent of the population size to the extent feasible. It will be more expensive, in some cases, on a per person basis to monitor very small systems, but such costs are not impractical for even the smallest community water system. However, in the case of man-made radioactivity, the nature of the potential hazard, the availability of laboratory facilities and the cost of monitoring do justify limiting required monitoring to large community water systems, serving more than 100,000 persons, community systems impacted by nuclear facilities, systems using water from major watersheds, and such other systems as are designated by the State.

Other groups pointed out that on the whole the monitoring cost per person served is trivial and objected to the aggregation of national costs in the preamble. EPA believes that the national costs as well as the cost to individual community water systems, are worthy of consideration.

One commentor believed that the number of community water systems impacted by nuclear facilities had been underestimated because the number of nuclear facilities would increase markedly in the future and many community water systems would be impacted by a single nuclear facility. It is true that the number of nuclear facilities that will necessitate monitoring of community water systems will increase in the future. The cost estimates in the preamble were based on an assumed average of one and a half community water systems being impacted by each nuclear facility. The commentor believed two would be impacted by each nuclear facility in his State.

Another commentor wanted to know if all drinking water regardless of source would be monitored for both alpha particle and beta particle radioactivity. The Regulations are specific on this point. Systems utilizing only ground water need not monitor for man-made beta particle radioactivity. Sources using surface water must monitor for both beta and alpha particle activity if they serve more than 100,000 persons, utilize surface water which may be contaminated by effluents from nuclear facilities, or as required by the State. Other surface water systems need not monitor for man-made radioactivity. However, it is recommended that all systems be monitored for gross beta particle activity.

A large number of respondents were concerned with the number and adequacy of existing monitoring facilities and the costs connected with establishing supplemental facilities. In some cases existing monitoring facilities may not be adequate. The situation will be more severe for those jurisdictions where the gross alpha particle concentration exceeds the screening level. However, the higher screen level in the revised regulation will reduce the number of mandatory radium analyses by a factor of two or more.

Moreover, the phased monitoring requirements imposed by these regulations should provide adequate time for State and private laboratories to add necessary facilities and equipment. It is true that many small systems will be required to monitor for gross alpha activity and, in the aggregate, bear the major cost impact of the monitoring requirements. However, it is precisely these systems which are most likely to be contaminated with natural radioactivity. There is no question but that additional funds will be required for such increased monitoring. It was the intent of Congress that these costs be borne by the individual public water systems and that corrective measures, such as consolidation of smaller systems, be employed to ameliorate this effect.

A few commentors questioned whether the proposed limits were "cost effective" in terms of both treatment and monitoring costs. As stated in the preamble to the proposed regulations, selection of an appropriate maximum contaminant level was not based solely on the estimated cost effectiveness of radium removal. As explained in the Statement of Basis and Purpose, the health risk estimates are uncertain by at least a factor of four. However, the difference in cost-effectiveness between different control levels is independent of this uncertainty and therefore provides information on where cost-benefit ratios become significantly poorer. The Statement of Basis and Purpose also examines why the cost-effectiveness of radium removal by ion exchange is low and suggests alternative approaches to obtaining maximum contaminant levels at lower costs. The cost-effectiveness of the required monitoring program will depend on the number of supplies identified as exceeding the maximum contaminant limits. This cannot be forecast until the initial monitoring is completed. In any event, a strict cost-effectiveness approach is not the intent of the Safe Drinking Water Act. Maximum contaminant levels are to prevent adverse health effects to the extent feasible.

One commentor interpreted a statement in the Preamble concerning future review of these regulations to indicate that the purpose of the Proposed Regulations was to conduct a national field survey for radioactivity in drinking water at State expense. A second comment expressed a similar opinion regarding monitoring requirements for man-made radioactivity.

The Proposed Regulations are based on the Administrator's determination that they protect health to the extent feasible after taking treatment costs into consideration. He is aware that the Agency's estimates of national cost are dependent on the number of community water systems impacted and that an adequate estimate of their number is not available now. By Congressional mandate these are interim regulations subject to revision in 1978. The Administrator would be remiss if he were to ignore new data on the impact of these regulations as it becomes available as an outgrowth of the reporting requirement.

Another commentor asked why the Agency had not set the limit for man-made radioactivity using a cost-benefit approach. The Agency does not believe such an approach is either practicable or needed at this time. Present levels of man-made radioactivity in community water systems are quite low—a statement supported in Appendix III of the Statement of Basis and Purpose and there is no evidence that allowing higher concentrations in drinking water would confer significant reductions in compliance costs. Effluent control costs are not likely to be changed by the proposed regulations for man-made radioactivity. Effluent control practices of the nuclear industry as currently regulated appear to be adequate in terms of the proposed maximum contaminant limits. The Agency does not believe it was the intention of Congress that the cost of removing man-made radioactivity from public water systems should be balanced against the cost of effluent controls required by regulations established under other legislation.

Calculational models used

One commentor objected to the statement in the preamble concerning the estimated dose due to drinking water contaminated by currently operating nuclear fuel cycle components. The objection was based on two points.

(1) That these estimates were based on calculational models, which may not accurately reflect reality.

(2) That the estimates do not consider aerial depositions from radioactive materials which are initially deposited into air and then fall out onto the ground and are washed into waterways.

The Administrator believes the best calculational models currently available were used for these estimates. Measurement of the actual doses is, of course, impossible at these low levels. As stated in the Statement of Basis and Purpose, the Administrator will consider new models as they are proposed by appropriate organizations and modify the proposed regulations as necessary to reflect new information as it becomes available. By basing compliance with maximum contaminant levels on measured concentrations of radioactivity in finished drinking water the Administrator believes aerial deposition as a source of water contamination is adequately considered.

Public water systems impacted

One commentor stated that the monitoring data included in the Statement of Basis and Purpose for community water systems were not representative of the radium or alpha particle radioactivity in sections of the country having abnormally high concentrations of natural radioactivity and therefore EPA's estimates of the impact of the proposed regulations were unrealistic. The Agency believes that the data given in the Appendix to the Statement of Basis and Purpose were representative of the country as a whole, but agrees there are sections of the country which routinely have higher amounts of radium in their community water systems. However, as stated in the Statement of Basis and Purpose, these national data were not used as a basis for the EPA estimate of the number of public water systems impacted by the proposed maximum contaminant limit for radium. Rather, that estimate is based on other monitoring data obtained mostly in regions where significant amounts of radium are commonly found in community water systems, as referenced in the Statement.

Linear nonthreshold response functions

One commentor stated the Agency was too conservative in the estimation of possible health effects because a linear nonthreshold dose response function was assumed. Another commentor stated a linear nonthreshold relationship is not conservative enough since an increased radiocarcinogenic response has been associated with low dose rates from alpha particle irradiation. Conversely, one commentor stated that there is a threshold for radiation injury from ingested radium and that the maximum contaminant level for radium should be based on his value for a threshold dose. Reasons for using a linear nonthreshold dose response were given in full in the Statement of Basis and Purpose and are reproduced here as Part III of this Appendix. The Agency is aware that one study on the results of clinical treatments with radium-224 indicates that protraction of the alpha exposure is more carcinogenic and that it has been hypothesized that lung cancer may be associated with very low dose rates from alpha particle emitters. Also, analyses of the radium dial painter data have been interpreted as indicating that bone cancers from lower radium doses occur later in life than from large doses and this has been interpreted as an argument for an effective threshold. However, the United States Public Health Service has studied this question in some detail, BRH/DBE 70-5, and EPA agrees with the USPHS finding that the data are insufficient to specify an unequivocal dose response model and their conclusion that, "* * * in the low dose region expected to be experienced by the general public, the assumption of a linear nonthreshold model continues to be a prudent public health philosophy for standards setting."

MISCELLANEOUS

Two States requested a definition of "nuclear facility." As explained in the Statement of Basis and Purpose, the term "nuclear facility" is flexible so that the States may determine which community water systems require additional monitoring. The term "nuclear facility" should not be construed as applying only to nuclear electric-generating plants and other components in the uranium fuel cycle but may also include, at the option of the State, waste storage areas, experimental facilities, and medical centers as outlined in the Statement of Basis and Purpose.

Four commentors believed that the proposed regulations would be difficult for persons working in community water systems to understand—that they were too technical. EPA agrees this is a highly technical subject not amenable to lay terms. However, the Agency has attempted to clarify the regulations and believes that all States have radiological health personnel who are willing to assist a supplier of water if particular problems of interpretation arise.

Several commentors expressed the opinion that data collected prior to implementation of the proposed regulations should be admissible as evidence of compliance. EPA agrees and the regulations have been modified so that analytical data acquired one year prior to the effective date of these regulations may be substituted for monitoring required during the initial period at the discretion of the State. This should reduce initial monitoring costs.

Two commentors expressed concern about adverse health effects that might occur as a result of sodium addition to water during the zeolite softening process. Possible health effects from sodium were considered in detail by the Agency in the development of the proposed regulations for inorganic chemicals, as well as for radium, and are discussed in the Statement of Basis and Purpose. The

Agency believes it not appropriate to set a maximum contaminant level for sodium. The consensus of opinion among medical personnel in this field is that, while the sodium added is not negligible, patients on a restricted, but noncritical, sodium diet would not be adversely affected at the increased levels contemplated. Patients for whom the increased levels might be critical are not normally permitted to use regular drinking water supplies but are restricted to specially processed water. The Statement of Basis and Purpose recommends that community physicians having patients in areas where the concentration of sodium is increased due to radium removal be so informed by the supplier.

One commentor took exception to the suggestion in the preamble that, taken as a whole, releases from hospitals and other industrial facilities would result in doses comparable to those released from nuclear facilities such as light water reactors. The statement in the preamble was not based on a full scale technical evaluation. The Agency is studying releases of radioactive materials from hospitals and other complexes through contractor research and will amend this estimate as necessary based on these and other findings.

Several respondents were in doubt as to the responsibilities of the water supplier in terms of actual performance of the required analyses. Allied questions were directed to whether the supplier of water or the State is responsible for the cost of analyses.

It is the intent of the regulations that the individual water supplier, while responsible for compliance with the regulations, may reasonably be expected to collect and transmit water samples to approved laboratories for actual performance of the radioanalysis. It is the intent of both Congress and these regulations that the principal costs associated with compliance with the Safe Drinking Water Act be borne by the individual public water systems. However, a State is not barred from analysing samples for public water systems without charge.

One commentor wanted to know if the proposed maximum contaminant levels for radioactivity in drinking water replaced Federal Radiation Council Guidance on Radiation Protection Guides for the general population. These regulations do not replace FRC recomendations on the transient intake of radioactive materials, which included both the food and water pathways, and which contemplated, except in the case of radium, exposures of less than a lifetime duration. EPA believes that the FRC Range II limit for large population groups cannot be applied to a single pathway, such as drinking water, since FRC Guides include exposure from external radiation, inhaled radioactivity and radioactivity in food as well as drinking water.

Three commentors questioned basing the maximum contaminant limits on the same dose limit whether applied to any internal organ or to the whole body. EPA has considered this question with care in developing these regulations, recognizing that the conservatism of the maximum contaminant limits was increased by this decision. The decision not to consider critical organs for the ingestion of radioactivity in drinking water is based on the National Committee on Radiation Protection (NCRP) recommendations contained in NCRP Report No. 39. In that report, the NCRP recommended that organ dose limits for the general population be based on whole body dose and not at a fraction of the corresponding occupational dose limit for critical organs. The NCRP decision was in part based on the lack of data available at that time to consider appropriately the risk from a radiation insult to various organs. Such data are becoming available now and the International Commission on Radiation Protection (ICRP) is considering basing dose limits on the risk to various organ systems. When the ICRP recommendations are developed in final form they will be considered by EPA.

PART III

ORP Policy Statement on the Relationship Between Radiation Dose and Effect; March 3, 1975

The actions taken by the Environmental Protection Agency to protect public health and the environment require that the impacts of contaminants in the environment or released into the environment be prudently examined. When these contaminants are radioactive materials and ionising radiation, the most important impacts are those ultimately affecting human health. Therefore, the Agency believes that the public interest is best served by the Agency providing its best scientific estimates of such impacts in terms of potential ill health.

To provide such estimates, it is necessary that judgments be made which related the presence of ionising radiation or radioactive materials in the environment, i.e., potential exposure, to the intake of radioactive materials in the body, to the absorption of energy from the ionising radiation of different qualities, and finally to the potential effects on human health. In many situations the levels of ionising radiation or radioactive materials in the environment may be measured directly, but the determination of resultant radiation doses to humans and their susceptible tissues is generally derived from pathway and metabolic models and calculations of energy absorbed. It is also necessary to formulate the relationship between radiation dose and effects; relationships derived primarily from human epidemiological studies but also reflective of extensive research utilising animals and other biological systems.

Although much is known about radiation dose-effect relationships at high levels of dose, a great deal of uncertainty exists when high level dose-effect relationships are extrapolated to lower levels of dose, particularly when given at low dose rates. These uncertainties in the relationships between dose received and effect produced are recognised to relate, among many factors, to differences in quality and type of radiation, total dose, dose distribution, dose rate, and radiosensitivity, including repair mechanisms, sex, variations in age, organ, and state of health. These factors involve complex mechanisms of interaction among biological chemical, and physical systems, the study of which is part of the continuing endeavor to acquire new scientific knowledge.

Because of these many uncertainties, it is necessary to rely upon the considered judgments of experts on the biological effects of ionising radiation. These findings are well-documented in publications by the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), the National Academy of Sciences (NAS), and the National Council on Radiation Protection and Measurements (NCRP), and have been used by the Agency in formulating a policy on relationship between radiation dose and effect.

It is the present policy of the Environmental Protection Agency to assume a linear, nonthreshold relationship between the magnitude of the radiation dose received at environmental levels of exposure and ill health produced as a means to estimate the potential health impact of actions it takes in developing radiation protection as expressed in criteria, guides, or standards. This policy is adopted in conformity with the generally accepted assumption that there is some potential ill health attributable to any exposure to ionising radiation and that the magnitude of this potential ill health directly proportional to the magnitude of the dose received.

In adopting this general policy, the Agency recognises the inherent uncertainties that exist in estimating health impact at the low levels of exposure and exposure rates expected to be present in the environment due to human activities, and that at these levels the actual health impact will not be distinguishable from natural occurrences of ill health, either statistically or in the forms of ill health present. Also, at these very low levels, meaningful epidemiological studies to prove or disprove this relationship are difficult, if not practically impossible to conduct. However, whenever new information is forthcoming, this policy will be reviewed and updated as necessary.

It is to be emphasised that this policy has been established for the purpose of estimating the potential human health impact of Agency actions regarding radiation protection, and that such estimates do not necessarily constitute identifiable health consequences. Further, the Agency implementation of this policy to estimate potential human health effects presupposes the premise that, for the same dose, potential radiation effects in other constituents of the biosphere will be no greater. It is generally accepted that such constituents are not more radiosensitive than humans. The Agency believes the policy to be a prudent one.

In estimating potential health effects it is important to recognise that the exposures to be usually experienced by the public will be annual doses that are small fractions of natural background radiation to at most a few times this level. Within the U.S. the natural background radiation dose equivalent varies geographically between 40 to 200 mrem per year. Over such a relatively small range of dose, any deviations from dose-effect linearity would not be expected to significantly affect actions taken by the Agency, unless a dose-effect threshold exists.

While the utilization of a linear, nonthreshold relationship is useful as a generally applicable policy for assessment of radiation effects, it is also EPA's policy in specific situations to utilize the best available detailed scientific knowledge in estimating health impact when such information is available for specific types of radiation, conditions of exposure, and recipients of the exposure. In such situations, estimates may or may not be based on the assumptions of linearity and a nonthreshold dose. In any case, the assumptions will be stated explicitly in any EPA radiation protection actions.

The linear hypothesis by itself precludes the development of acceptable levels of risk based solely on health considerations. Therefore, in establishing radiation protection positions, the Agency will weigh not only the health impact, but also social, economic and other considerations associated with the activities addressed.

[FR Doc.76-19006 Filed 7-8-76;8:45 am]

APPENDIX 3

NBS STANDARD REFERENCE MATERIALS

Radioactivity Standards

Information concerning the SRM appears on it or its container. A Certificate containing pertinent information on the SRM is sent under separate cover; a photocopy of the certificate is sent with the SRM. Copies of these Certificates and information concerning the applications of these SRM's are available on request to the NBS Office of Standard Reference Materials. These Materials (except the carbon-14 contemporary dating standard) are shipped only by express or air freight (shipping charges collect). The prices of SRM's may change as current stocks are depleted and are replaced. Purchasers will be billed at the prices in effect at the time of shipment.

The stated accuracies of the older standards are, in general, an estimate of the standard deviation added to an estimate of maximum possible systematic error. The accuracies of more recent standards are based on the 99 percent confidence level of precision, with the same estimate of systematic error.

The International Commission on Radiation Units (ICRU) recommended definition of the activity (A) of a quantity of a radioactive nuclide is the quotient of ΔN by Δt, where ΔN is the number of nuclear transformations that occur in this quantity, in time Δt: $(A = \Delta N/\Delta t)$. NBS uses the abbreviation ntps for nuclear transformation per second. In this list both ntps and dps are used; the latter when dps has been used in certificates printed before 1968. The terms: αps, β^-ps, β^+ps, K-x-rays ps, γps are used for the emission rates of alpha particles, beta particles, positrons, K-x-rays, and gamma-rays, respectively.

The SRM's listed below, not marked with an asterisk (*), may be ordered singly, without a license, under the general licensing provisions of the Atomic Energy Act of 1954. Those marked by an asterisk are available only under the special licensing provisions of the Atomic Energy Act of 1954.

NOTE: Certain radionuclides are not economical to maintain in stock because of short half lives or low demand. When sufficient demand exists, based on letters of inquiry, these materials are prepared and those who have expressed interest are notified of their availability. A representative list of such radionuclides is given on page If you need any of these radionuclides or others not listed, contact the Radioactivity Section, Room C114, Radiation Physics Building, National Bureau of Standards, Washington, D.C. 20234 (Telephone: 301–921-2668).

In addition, chemically stable solutions of most radionuclides, including those no longer issued by NBS or that are currently out of stock, may be submitted to NBS for calibration as described in "Calibration and Test Services of the National Bureau of Standards," NBS Special Publication 250. Requests for these tests should be submitted, with full source information for approval of suitability, to the Radioactivity Section.

Alpha-Particle Standards

These SRM's consist of a practically weightless deposit of the nuclide on a thin platinum foil cemented to a monel disk.

SRM	Radionuclide	Approximate Activity at Time of Calibration (Month, Year)	Accuracy (%)
*4906	Plutonium-238	1.4×10^3 to 3.4×10^4 ntps (4/69)	±0.8
4904-D	Americium-241	2×10^3 to 5×10^4 ntps (2/70)	1.0
4907	Gadolinium-148	50 to 2×10^4 ntps (1/73)	1.7

Beta-Particle and Gamma-Ray Gas Standards

These SRM's contain the Radionuclide in the inactive gas at a pressure of about one atmosphere in a glass break-seal ampoule.

SRM	Radionuclide	Approximate Activity at Time of Calibration (Month/Year)	Uncertainty (%)
4935-C	Krypton-85	5×10^7 ntps/mol (3/74)	1.0
*4235	Krypton-85	1×10^7 ntps/source (11/74)	1.0

APPENDIX 3

Alpha-Particle, Beta-Particle, Gamma-Ray, and Electron-Capture Solution Standards

These standard reference materials are contained in flame-sealed ampoules.

SRM	Radionuclide	Approximate Activity or Emission Rate per gram of Solution at Time of Calibration (Month, Year)	Approx. Weight of Solution (gram)	Accuracy (%)
4229	Aluminum-26	39 ntps (11/71)	4.6	1.1
4219	Cadium-109	1×10^5 γps		
*4233	Cesium-137	5×10^{14} atoms (12/72)	5.1	0.5
4925	Carbon-14 (benzoic acid in toluene)	2×10^4 dps (7/58)	3	2.4
4222	Carbon-14 (n-hexadecane)	4×10^4 dps (6/67)	3	3.1
4223	Carbon-14 (n-hexadecane)	4×10^3 dps (6/67)	3	3.1
4224	Carbon-14 (n-hexadecane)	4×10^3 dps (6/67)	3	3.1
4245	Carbon-14 (sodium carbonate)	4×10^5 dps (5/74)	5	1.0
4246	Carbon-14 (sodium carbonate)	4×10^4 ntps (5/74)	5	0.9
4247	Carbon-14 (sodium carbonate)	4×10^3 ntps (5/74)	5	1.1
4943	Chlorine-36	1×10^4 β^-ps (1962)	3	2.3
4941-D	Cobalt-57	6×10^5 ntps (5/73)	5	1.8
4926	Hydrogen-3 (H_2O)	9×10^5 dps (9/61)	25	1.9
4927	Hydrogen-3 (H_2O)	9×10^5 dps (9/61)	3	1.9
4947	Hydrogen-3 ($C_6H_5CH_3$)	3×10^5 dps (2/64)	4	1.0
*4949	Iodine-129	0.2 μCi (1973)	1.1	1.7
4929-C	Iron-55	2×10^4 K-x-ray ps (4/70)	3.9	2.7
*4226	Nickel-63	2×10^5 ntps (5/68)	4.1	1.0
4940-B	Promethium-147	5×10^4 dps (11/67)	3	1.9
4228-B	Selenium-75	1×10^4 ntps (4/74)	5	2.9
4232	Silver-110m	1.7×10^5 ntps (8/74)	5	0.7
4921-C	Sodium-22	1×10^4 β^+ps (8/64)	2.8	1.4
4922-E	Sodium-22	2×10^5 β^+ps (3/67)	5.1	1.4

Contemporary Standard for Carbon-14 Dating Laboratories

SRM	Description
4990-B	Oxalic acid; no specific activity is given. (One pound of oxalic acid taken from specially prepared material for use as a common contemporary standard against which world-wide measurements can be compared.)

NOTE: These SRM's are shipped parcel post, prepaid to domestic and overseas purchasers.

Environmental Standards

SRM	Radionuclide(s)	Approximate Gamma Ray Emission Activity (Month/Year)	Form	Unit	Uncertainty (%)
4215-B	Mixed Radionuclides	1×10^5 γps (7/74)	Point Source	+[1]	–
4216-B	Mixed Radionuclides	4×10^4 γps (7/74)	Point Source	+[1]	–
*4332	Americium-243	135 ntps/g (9/74)	Solution	2g	1.4
*4333	Americium-243	3 ntps/g (9/74)	Solution	5g	1.5
*4330	Plutonium-239	50 ntps/g (1974)	Solution	2g	< 3%
4331	Plutonium-239	5 ntps/g (1974)	Solution	2g	< 3%

[1] These SRM's contain: cadmium-109, cobalt-57, cerium-139, mercury-203, tin-113-indium-113m, strontium-85, cesium-137-barium-137m, yttrium-88, and cobalt-60. They are prepared by depositing the radioactive material on polyester tape and covering it with a layer of the same tape, mounted on an aluminum ring.

Low Energy Photon Sources*

SRM	Type	Approximate Emission Rate Per Steradian at Time of (Month/Year)	Uncertainty (%)
4260	Iron-55	200-400 K-X-Rays (3/74)	3.0

*These SRM's consist of a thin-layer deposit of the radionuclide on a thin stainless steel or platinum foil cemented to a monel disk.

APPENDIX 3

Gamma-Ray "Point-Source" Standards

This group of Standard Reference Materials is usually prepared by depositing the radioactive material and sealing it between two layers of polyester tape, mounted on an aluminum ring. Exceptions to this procedure are americium, krypton, and thorium SRM's. The americium-241 SRM's, 4211 and 4213, are prepared by electroplating americium onto a 0.010-cm thick platinum foil, which is covered with a 0.005-cm thick aluminum foil. The aluminum-covered source is sandwiched between two layers of 0.036-cm thick polyurethane film tape. The krypton-85 SRM, 4212, is prepared by sealing a krypton-85 impregnated aluminum foil between two glass disks, with an epoxy adhesive. The thorium-228 SRM's, 4205 and 4206, are prepared by depositing and sealing the radionuclide between two layers of gold foil and this sandwich is then sealed between two double layers of polyurethane-film tape.

SRM	Radionuclide	Gamma-Ray Energy (mev)	Approximate Activity (ntps) at Time of Calibration (Month/Year)	Uncertainty (%)
*4211	Americium-241	0.060	4 to 18 × 10^4 (2/70)	2.8
*4213	Americium-241	0.060	2 to 4 × 10^5 (2/70)	2.8
4202-B	Cadmium-109	0.088	1 to 2 × 10^5 (5/74)	1.9[1]
4214	Cobalt-57	0.122, 0.136	1 × 10^4 to 1 × 10^6 (3/73)	1.7
4999-E	Cerium-139	0.166	9 × 10^4 to 2 × 10^6 (11/73)	2.2
*4212	Krypton-85	0.514	7 × 10^6 to 4 × 10^7 (5/71)	2.6
4200-B	Cesium-137	0.662	7 × 10^4 (12/68)	1.3
*4207	Cesium-137	0.662	5 × 10^6 (12/68)	1.3
4201-B	Niobium-94	0.702, 0.871	4 to 6 × 10^5 (4/70)	1.5
4240	Bismuth-207	0.5696, 1.0634, 1.7697	5 × 10^4 to 1 × 10^6 (1/73)	1.4
4203-C	Cobalt-60	1.173, 1.332	1 to 2 × 10^5 (2/73)	1.2
4210	Cobalt-60	1.173, 1.332	2 × 10^6 (4/69)	1.1
4217	Silver-110m		1 to 2.5 × 10^4 (8/74)	1.0
4991-C	Sodium-22	1.2745	6 × 10^4 (4/69)	1.5
4996-B	Sodium-22	1.2745	3 × 10^3 (4/69)	1.5
4209-B	Yttrium-88	0.898, 1.836	2 to 5 × 10^5 (10/73)	1.8

[1] Uncertainty in X-ray emission rate (uncertainty in activity is 3.9%).

Radium Gamma-Ray Solution Standards

These samples are contained in flame-sealed glass ampoules.

SRM	Radium Content (in micrograms)	Accuracy (%)
4955	0.1	±3.6
4956	0.2	4.4
4957	0.5	1.8
4958	1.0	1.8
4959	2.0	1.3
4960	5.0	1.3
4961	10	1.1
4962	20	1.1
4963	50	1.1
4964-B	102	0.5

Radium Solution Standards for Radon Analysis

These samples are contained in flame-sealed glass ampoules.

SRM	Approximate Radium Content (gram)	Approx. Wt. Soln. (grams)	Accuracy (%)
4951	10^{-11}	100	±1.0
4950-B	10^{-9}	20	1.0
4953	10^{-8}	20	1.0
4952-B	Blank Solution	(In Preparation)	

APPENDIX 3

Radioactivity Standard Reference Materials Currently Not in Stock

Radionuclide	Forms	Status	Radionuclide	Forms	Status
Americium-241	Solution,		Niobium-95	Point Source, Solution	C, F
	Low energy photon source	A	Phosphorus-32	Solution	C, F
Argon-37	Gas	B	Plutonium-242	Solution	A
Argon-39	Gas	E	Polonium-210	Plated Source	D
Barium-140	Solution	E	Potassium-42	Solution	C, F
Cadmium-109	Solid,		Scandium-46	Solution	C, F
	Low energy photon source	E	Sodium-24	Solution	C, F
Calcium-45	Solution	C, F	Strontium-85	Point Source, Solution,	A, F
Cerium-141	Solution	C, F		Low energy photon source	E
Cerium-144	Solution	A, F	Strontium-89	Solution	C, F
Chromium-51	Point Source, Solution	C, F	Strontium-90	Solution	C, F
Gold-198	Solution	C, F	Sulfur-35	Solution	C, F
Iodine-125	Solution	C	Tantalum-182	Solution	F
Iodine-131	Solution	C, F	Thallium-204	Solution	F
Iron-59	Solution	C, F	Thorium-228	Point Source	A
Manganese-54	Point Source	C, F	Thorium-229	Solution	A
Mercury-197	Solution	C, F	Tin-113	Solution	C, F
Mercury-203	Point Source, Solution	C, F	Xenon-133	Gas	B
Molybdenum-99	Solution	E	Zinc-65	Point Source, Solution	C, F

A. In preparation.
B. Issued periodically.
C. Issued when sufficient demand is demonstrated.
D. Prepared on request.
E. Under development.
F. See, Calibration and Test Services of the National Bureau of Standards, SP250.

Metallurgical Standards

This SRM is intended for calibrating x-ray diffraction equipment to determine the relative amounts of iron carbide in steel.

SRM	Type	Form
493	Spheroidized Iron Carbide (Fe_3C) in Ferrite	Wafer: 29 x 29 x 2.4 mm

Mossbauer Standards

These SRM's are issued for the calibration of the isomer shift of iron compounds and alloys and to provide a uniform basis for presentation of mossbauer isomer shift data.

SRM	Type	Form
725	Sodium Pentacyanonitrosylferrite II (Sodium Nitroprusside) for Isomer Shift of Iron Compounds	Platelet: 1 x 1 x 0.0775 cm
1541	Iron Foil	Foil: 2.5 cm x 2.5 cm x 23 μm

X-ray Diffraction Standard

SRM 640 is a powdered silicon material to be used as an internal standard for powder diffraction measurements. The lattice parameter has been accurately determined at 25.0 °C using a high angle goniometer and the NBS tungsten internal standard. The use of SRM 640 will allow the results to be coupled to Powder Diffraction File (when converted to the same wavelength) based on the NBS internal standards of 1966. The weighted average of the lattice parameter, $\bar{a}$, uncorrected for refraction is 5.43088 Å and the standard error is estimated to be 3.5×10^{-5} Å.

SRM	Type	Unit Size
640	Silicon Powder	10 g

APPENDIX 4

NBS STANDARDS

ALPHA-PARTICLE STANDARDS

Radionuclide	Approx. α-particle-emission rate into 2π geometry and/or approx. activity at time of calibration (s^{-1})	(month/year)	Overall uncertainty (%)	SRM No.	Unit price ($)	Notes
Americium-241	2×10^3 to 5×10^4	2/70	±1.0	4904-D	132	2,6
Gadolinium-148	50 to 2×10^4	1/73	1.7	4907	100	2
Plutonium-238	1×10^3 to 3×10^4	4/69	0.8	4906	166	2,7
Polonium-210	made to order: 100α		~ 1	4900		1, 29
	200α			4901		1, 29

BETA-PARTICLE AND GAMMA-RAY GASEOUS STANDARDS

Radionuclide	Approx. activity, or emission rate, at time of calibration (s^{-1})	(month/year)	Approx. volume (ml)	Overall uncertainty (%)	SRM No.	Unit price ($)	Notes
Argon-37	900	4/75	10	±1.8	4300-B	100	21
Argon-37	110	4/75	10	2.8	4301-B	100	21
Argon-39	3.3×10^4	7/75	10	1.5	4302	137	21
Argon-39					4303		25
Krypton-85	5×10^7 per mole	3/74	10	0.9	4935-C	108	4
Krypton-85	9×10^6 to 1.5×10^7	11/74	3	1.2	4235	108	4
Krypton-85	2×10^3 514-keVγs^{-1}	4/75	34.5	3.7	4308	106	29,17,22
Krypton-85(ambient)					4309		25
Xenon-127					4310		23
Xenon-131m					4305		24
Xenon-133					4306		3, 24
Xenon-133					4307		5, 24

CONTEMPORARY STANDARD FOR CARBON-14 DATING LABORATORIES

ALPHA-PARTICLE, BETA-PARTICLE, GAMMA-RAY AND ELECTRON-CAPTURE SOLUTION STANDARDS

Radionuclide	Approximate activity, or emission rate, per gram, at time of calibration (month/year)		Approximate weight of solution	Overall uncertainty	SRM No.	Unit price	Notes
	(s^{-1} g^{-1}) exceptions noted		(g)	(%)		($)	
Aluminum-26	39	11/71	4.6	±1.1	4229	208	8, 29
Americium-243	134	9/74	2	1.4	4332	102	8
Americium-243	3	9/74	5	1.5	4333	102	8
Cadmium-109							8, 30
Carbon-14(Na_2CO_3 in H_2O)	4×10^5	5/74	5	1.0	4345	102	8, 29
Carbon-14(Na_2CO_3 in H_2O)	4×10^4	5/74	5	0.9	4246	102	8, 29
Carbon-14(Na_2CO_3 in H_2O)	4×10^2	5/74	5	1.1	4247	102	8, 29
Carbon-14(C_6H_5COOH in $C_6H_5CH_3$)	2×10^4	7/58	3	2.4	4925	56	8, 29
Carbon-14($C_{16}H_{34}$)	4×10^4	6/67	3	3.1(*)	4222	63	8, 29
Carbon-14($C_{16}H_{34}$)	4×10^3	6/67	3	3.1(*)	4223	63	8, 29
Carbon-14($C_{16}H_{34}$)	4×10^2	6/67	3	3.1(*)	4224	63	8, 29
Cerium-praseodymium-144					4948		8, 30
Cesium-137-Barium-137m	4.6×10^{14} (Atoms g^{-1})	12/72	5.2	0.5	4233	103	8, 26
Chlorine-36	1×10^4 (β^-)	1962	3	2.3	4943	51	8, 29
Chromium-51					4230		31
Cobalt-57					4941-D		8, 30
Cobalt-57					4408L		8, 30
Cobalt-60	1.0×10^5	5/75	5.1	1.1	4913-B	125	8
Cobalt-60	5.5×10^5	5/75	5.1	1.1	4915-B	125	8
Hydrogen-3(H_2O)	9×10^3	9/61	25	1.5	4926	56	8, 29
Hydrogen-3(H_2O)	9×10^5	9/61	3	1.5	4927	56	8, 29
Hydrogen-3($C_6H_5CH_3$)	3×10^5	2/64	4	1.0	4947	54	8, 29
Iodine-125					4944		24
Iodine-129	7×10^3	1973	1.1	1.7	4949	90	8
Iron-55	2×10^4 (kx)	4/70	3.9	2.7	4929-C	123	8
Mercury-197					4221		8, 31
Mercury-203					4932		8, 31
Nickel-63	2×10^6	5/68	4.1	1.0	4226	157	8
Niobium-95					4937		8, 31
Polonium-210	2.8×10^3 (α)	8/68	3.1	1	4336	120	8
Plutonium-239					4330		8, 31
Plutonium-239	6 (α)	3/75	2	1.0	4331	122	8
Plutonium-242	21	3/75	2	1.0	4334	108	8
Plutonium-242	2	3/75	5	1.1	4335	108	8

ALPHA-PARTICLE, BETA-PARTICLE, GAMMA-RAY AND ELECTRON-CAPTURE SOLUTION STANDARDS
(continued)

Radionuclide	Approximate activity, or emission rate, per gram, (s^{-1} g^{-1}) exceptions notes	at time of calibration (month/year)	Approximate weight of solution (g)	Overall uncertainty (%)	SRM No.	Unit price ($)	Notes
Promethium-147	5×10^4	11/67	3	1.9	4940-B	68	8, 29
Selenium-75					4228-B		30
Selenium-75	8.5×10^5	10/75	5	2.5	4409L	125	8
Silver-110m-							
Silver-110	1.7×10^5	8/74	5	0.7	4232	116	8
Sodium-22					4921-C		30
Sodium-22	2×10^5 (β^+)	3/67	5.1	1.4(*)	4922-E	69	8
Strontium-85	8.8×10^5	10/75	4.8	1.2	4403-L	125	8
Strontium-89					4945		31
Strontium-Yttrium-90	4.0×10^3	4/75	2.9	2.1	4919-D	100	8, 14
Strontium-Yttrium-90	1.3×10^6	8/75	3.1	1.5	4234	107	8
Thorium-229					4227		8, 23
Tin-113-Indium-113m	9.5×10^5 (391.7keVγ)	7/75	5.4	2.6	4402PL	100	8
Zinc-65					4930-E		8, 23
Mixed Radionuclides					4242-E		30
Mixed Radionuclides					4243-E		30
Mixed Radionuclides					4254		30

* 99.73% Confidence Level

GAMMA-RAY "POINT-SOURCE" STANDARDS

THESE SRM's ARE LISTED IN ORDER OF ASCENDING GAMMA-RAY ENERGIES (EXCEPT THE LAST TWO) TO FACILITATE SELECTION OF A SUITABLE SOURCE.

Radionuclide	Gamma-ray energy (MeV)	Approximate activity, s^{-1}, at time of calibration (month/year) (except mixed radionuclides = γs^{-1})		Overall uncertainty (%)	SRM No.	Unit price ($)	Noates
Americium-241	0.060	4.0 to 18×10^4	(2/70)	±2.8	4211	136	15, 19
Americium-241	0.060	1.9 to 4.1×10^5	(2/70)	2.8	4213	136	15, 19
Cadmium-109	0.088						30
Cobalt-57	0.122, 0.136				4214		31
Cerium-139	0.166						30
Mercury-203	0.279				4995		31
Mercury-203	0.279				4208		31
Chromium-51	0.320				4204		31
Krypton-85	0.514	6.5 to 36.5×10^6	(5/71)	2.6	4212	168	16, 19
Silver-110m-Silver-110	0.658,0.885, etc.	1 to 2.5×10^4	(8/74)	1.0	4217	116	10,19,29
Cesium-137-Barium-137m	0.662	7×10^4	(12/68)	1.3	4200-B	68	10, 29
Cesium-137-Barium-137m	0.662	5×10^5	(12/68)	1.3	4207	68	10
Niobium-94	0.702, 0.871	4 to 6×10^3	(4/70)	1.5	4201-B	160	10, 19
Niobium-95	0.765				4993		31
Manganese-54	0.835				4997		31
Zinc-65	1.115				4992		31
Bismuth-207	0.5696, 1.0634 1.7697	5.4 to 11×10^4	(1/73)	1.4	4240	147	10, 19
Cobalt-60	1.173, 1.333	1.0 to 2.3×10^5	(2/73)	1.2	4203-C	116	10, 19
Cobalt-60	1.173, 1.333	2×10^6	(4/69)	1.1	4210	94	10
Sodium-22	1.2745	6×10^4	(4/69)	1.5	4991-C	87	10
Sodium-22	1.2745	3×10^5	(4/69)	1.5	4996-B	87	10
Yttrium-88	0.898, 1.836						31
Yttrium-88	0.898, 1.836						31
Thorium-228	2.614	6×10^4	(8/68)	2.2	4205	106	12
Thorium-228	2.614				4206		10,12,23
Mixed Radionuclides	0.088-1.836	7×10^4 γs^{-1} (total)	(10/75)	3	4215-C	100	10, 11
Mixed Radionuclides	0.088-1.836	3.5×10^4 γs^{-1} (total)	(10/75)	3	4216-C	100	10, 11

LOW-ENERGY PHOTON STANDARDS: X-RAY EMISSION RATE STANDARDS
POINT SOURCES

Radionuclide	Emission rate at time of calibration (month/year)		Overall uncertainty (%)	SRM No.	Unit price ($)	Notes
Americium-241				4262		23
Cadmium-109				4261	102	23
Iodine-125	5×10^{5} $(\mathrm{kx} + \gamma)\mathrm{s}^{-1}$	2/76	2.0	4265	102	10
Iron-55	200 to 400 kxs^{-2}/steradian	3/74	3.0	4260	102	18,19,29
Strontium-85	4.5×10^{4} to 8.8×10^{4} kxs^{-1}	7/75	2.5	4263	102	10, 19

ENVIRONMENTAL STANDARDS

Form	Radionuclides		Approximate activity, or emission rate, per gram at time of calibration (month/year) $(\mathrm{s}^{-1}\mathrm{g}^{-1})$	Approx. weight (g)	Overall uncertainty (%)	SRM No.	Unit price ($)	Notes
River sediment	Certified	^{40}K, ^{54}Mn, ^{60}Co, ^{65}Zn, ^{90}Sr, ^{90}Y, ^{137}Cs, ^{152}Eu, ^{154}Eu, ^{228}Ac, ^{239}Pu, ^{240}Pu	<1 per radionuclide (1/75)	100	4.5-19.1	4350	162	20
	Values given, but uncertified	^{55}Fe, ^{125}Sb, ^{155}Eu, ^{208}Tl, ^{212}Pb, ^{212}Bi, ^{214}Pb, ^{214}Bi, ^{226}Pa, ^{228}Th, ^{230}Th, ^{232}Th, ^{231}Pa, ^{234}U, ^{235}U, ^{238}U, ^{238}Pu, ^{241}Am, ^{244}Cm	<1 per radionuclide					

RADIUM SOLUTION STANDARDS FOR RADON ANALYSIS

Nominal radium content (month/year) (g)		Approximate weight of solution (g)	Overall uncertainty (%)	SRM No.	Unit price ($)	Notes
Blank solution				4952		30
10^{-11}				4951		30
10^{-9}				4950		30
10^{-8}	(3/68)	20.6	1.0	4953	89	8

RADIUM-226 GAMMA-RAY SOLUTION STANDARDS

Nominal radium content (month/year) (μg)		Approximate weight of solution (g)	Overall uncertainty (%)	SRM No.	Unit price ($)	Notes
0.1	(9/67)	5.1	±3.6	4955	71	8
0.2	(9/67)	5.1	4.4	4956	71	8
0.5	(9/67)	5.1	1.8	4957	71	8
1.0	(9/67)	5.1	1.8	4958	71	8
2.0	(9/67)	5.1	1.3	4959	71	8
5.0	(9/67)	5.1	1.3	4960	71	8
10.0	(9/67)	5.1	1.1	4961	71	8
20.0	(9/67)	5.1	1.1	4962	71	8
50.0	(9/67)	5.1	1.1	4963	71	8
102.0	(6/65)	5.2	0.5	4964-B	71	8

APPENDIX 5

May, 1976

PRICE LIST FOR NBS RADIOACTIVITY STANDARD REFERENCE MATERIALS

Federal regulations require all suppliers of radioactive material to verify, prior to shipment, that the purchaser is authorized to receive the type, form, and quantity of material to be transferred.

WE REQUIRE THAT A LICENSE CERTIFICATION ACCOMPANY EVERY ORDER FOR RADIOACTIVITY STANDARDS. The form on the reverse page is a sample of the license certification, which, when completed, will satisfy the requirements for the specific purchase order.

This form may be duplicated as needed.

PLEASE HELP US TO EXPEDITE YOUR ORDER BY ADHERING TO THIS REQUIREMENT.

National Bureau of Standards
1/9/75

LICENSE CERTIFICATION

I hereby certify that ______________________________
(Licensee)

Is authorized to receive the following: ______________________________
(Type, form and quantity of radioactive material or SRM number)

____

License/Registration Certificate/Prime Contractor (cross out all but one) Number: _____ _________

Issuing Agency: ______________________________

Expiration Date: ______________________________

I further certify that I am authorized to act for and in behalf of

______________________________ to execute this certification.
(Licensee)

____
(Signature)

____
(Title)

____
(Date)

References:

Code of Federal Regulations
Title 10
Part 30.41
Part 40.51
Part 70.42

U. S. DEPARTMENT OF COMMERCE
National Bureau of Standards
Washington, D.C. 20234

October, 1975

CALIBRATION SERVICES, RADIOACTIVITY SECTION

REQUESTS FOR TESTS SHOULD BE SUBMITTED, WITH FULL DETAILS, FOR APPROVAL.

Direct inquiries to, and mark shipments for the attention of: Radioactivity Section, RAD PHY-C114, National Bureau of Standards, Washington, D.C. 20234. Telephone: 301-921-2665.

Calibration of gamma-ray emitting radioactive samples

Calibration of gamma-ray emitting radioactive samples that conform to the physical, chemical and activity level specifications for measurement in the National Bureau of Standards calibrated $4\pi\gamma$ ionization chamber.

ITEM	DESCRIPTION	FEE
8.2B	(1) 100-300 micrograms radium	$213.00
8.2C	(2) Chemically stable solutions of the following radionuclides in the specified activity ranges can be measured . . . . i. 50-100 microcuries sodium-22, sodium-24, scandium-46, cobalt-60, yttrium-88, silver-110_m-silver-110. ii. 100-300 microcuries manganese-54, iron-59, zinc-65, selenium-75, strontium-85, niobium-95, tin-113-indium-113m, iodine-131, cesium-137-barium-137m, tantalum-182, gold-198, mercury-203. iii. 200-600 microcuries potassium-42, cobalt-57, cerium-139, cerium-141, mercury-197. Solutions should be 5 ml in volume and flame-sealed in glass vials or ampoules (free of high Z elements) of O.D. 16.0 ± 0.5 mm, wall thickness approximately 0.5 mm. Ampoules, for this purpose, may be obtained from the Radioactivity Section.	$213.00
8.2D	Chemically stable solutions of the following radionuclides in the specified activity ranges can be measured . . . . i. 10-30 microcuries sodium-22, sodium-24, scandium-46, cobalt-60, yttrium-88, silver-110_m-silver-110 ii. 30-80 microcuries manganese-54, iron-59, zinc-65, selenium-75, strontium-85, niobium-95, tin-113-indium-113m, iodine-131, cesium-137-barium-137m, tantalum-182, gold-198, mercury-203. iii. 60-100 microcuries potassium-42, cobalt-57, cerium-139, cerium-141, mercury-197. iv. 200-1000 chromium-51, cadmium-109 Solutions should be 5 ml in volume and flame-sealed in glass vials or ampoules (free of high Z elements) of O.D. 16.0 ± 0.5 mm, wall thickness approximately 0.5 mm. Ampoules, for this purpose, may be obtained from the Radioactivity Section.	$242.00
	For tests not covered by the above schedule, fees will be charged dependent on time involved in making the tests.	

Calibration of Alpha-Particle Emitting Samples

Calibration of alpha-particle emitting samples that conform to the physical and activity specifications for measurement in the National Bureau of Standards 2πα-proportional or 1πα-scintillation counters; the preparation and calibration of polonium-210 sources; the calibration of alpha-particle samples in both the 2πα-proportional and the 1πα-scintillation counters, for 2π count-rate or activity, respectively.

ITEM	DESCRIPTION	FEE
8.2H	Chemically and physically stable samples that conform to the specifications listed below can be measured for total α-particle count rate into a 2π geometry using the N.B.S. 2π proportional counter . . . . i. Source diameter should not exceed 10 cm. ii. Source thickness should be such that more than 99.5% of the emitted alpha particles have an energy greater than 400 keV. iii. Activity should not exceed 0.3 microcuries. iv. Activity should not be less than 20 picocuries.	$214.00
8.2I	Samples that are chemically and physically stable can be measured for activity in the N.B.S. 1πα counter if they meet the specifications outlined in 8.2H. Activity should not be less than 3 nanocuries	$217.00
8.2J	Samples that are chemically and physically stable and meet the specifications outlined above in 8.2H and I can be measured in both the 2πα-proportional and the 1πα-scintillation counters.	$292.00
8.2K	Polonium-210 sources will be prepared on request, due to the relatively short half life, 138.4 days. These sources will consist of a practically weightless deposit of polonium-210 on a monel disk 2.54 cm in diameter and 0.16-cm thick and will be calibrated in either 2π or 1π geometry. . . . . i. Activity range: 0.5 - 3.0 nanocuries ii. Polonium-210 restricted to a 0.3 cm diameter area in the approximate center of disk. iii. These sources are unsuitable for prolonged use in a vacuum, due to possible loss or transfer of source material. iv. The total activity of these sources will be such that they may be ordered under the general licensing provisions of the Atomic Energy Act of 1954.	$213.00
	For special measurements not covered by this schedule, fees will be charged dependent on time involved in making the measurements.	

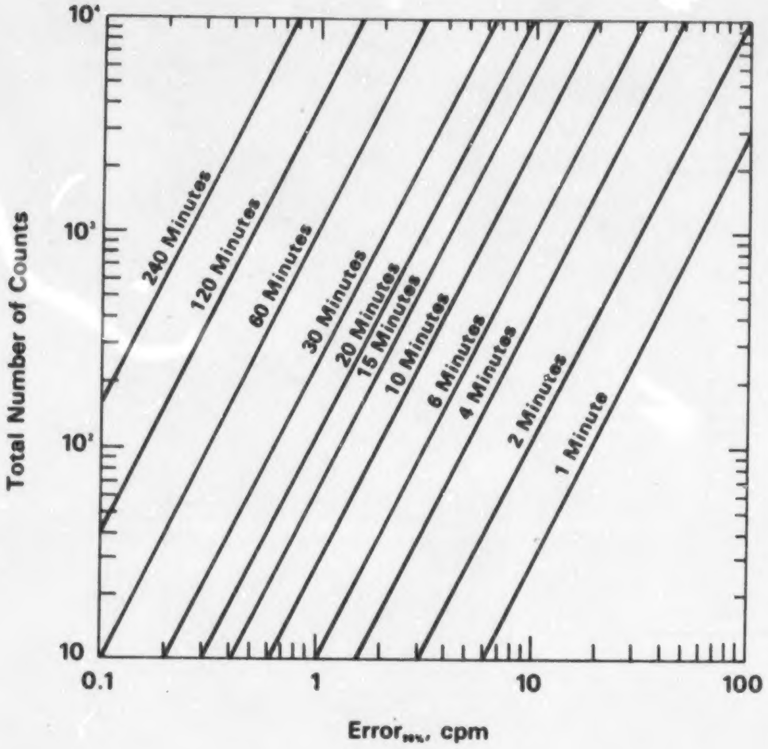
Calibration of beta-ray emitting radioactive samples

Calibration of beta-ray emitting radioactive samples that conform to the physical, chemical, and activity level specifications for measurement in either the National Bureau of Standards calibrated $2\pi\beta$ windowless proportional flow counter, or in the National Bureau of Standards calibrated $2\pi\beta$ ionization chamber.

ITEM	DESCRIPTION	FEE
8.2P	Chemically stable solutions of the following radionuclides in the specified activity ranges can be measured in the National Bureau of Standards calibrated $2\pi\beta$ windowless proportional flow counter. i. 1-10 microcuries/milliliter chlorine-36, strontium-yttrium-90. ii. 2-20 microcuries/milliliter thallium-204. iii. 5-50 microcuries/milliliter calcium-45, promethium-147. iv. 10-100 microcuries/millilieter sulfur-35. Solutions should be approximately 5 ml in volume and flame-sealed in glass vials or ampoules.	$462.00
8.2Q	Chemically stable solutions of the following radionuclides in the specified activity ranges can be measured in the National Bureau of Standards calibrated $2\pi\beta$ ionization chamber . . . . i. 2-20 microcuries/milliliter phosphorus-32. Solution should be neutral or weak acid with not more than 0.2 mg/ml total solids. ii. 2-20 microcuries/milliliter strontium-89, strontium-yttrium-90. Solution should be weak HCl (1N or less) with not more than 0.2 mg/ml total solids. Solutions should be approximately 5 ml in volume and flame-sealed in glass vials or ampoules.	$290.00
	For tests not covered by the above schedule, fees will be charged dependent on the time involved in making the tests.	

APPENDIX 6

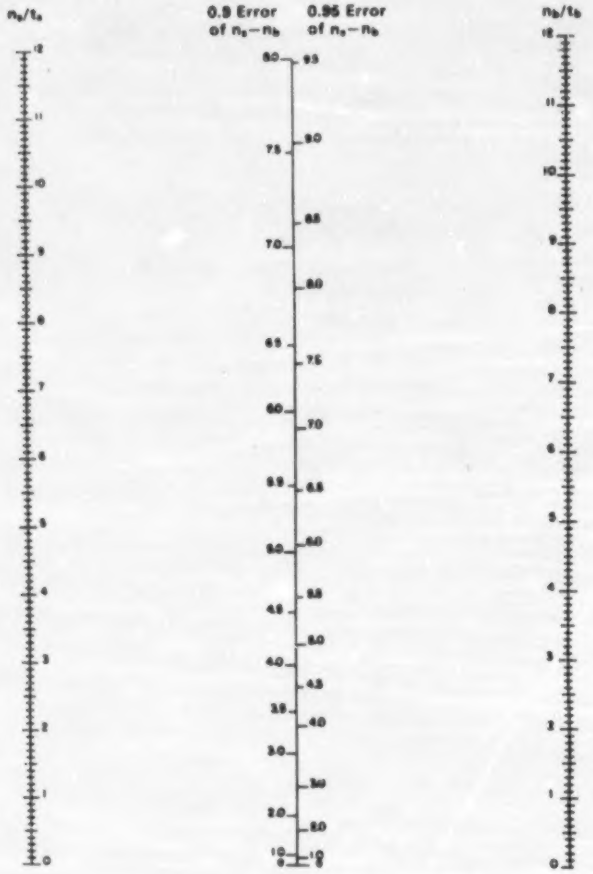
ERROR PLOTS AND STATISTICS OF COUNTING



Error in Counts per Minute
as a Function of Total Count and Length of Count.
(95% Confidence Level.)

APPENDIX 6

ERROR PLOTS AND STATISTICS OF COUNTING



Nomogram for 0.9 and 0.95 Error of Low Counting Rates.
(Jarrett, AECU-262, Mon P-126.)

Explanation of Symbols

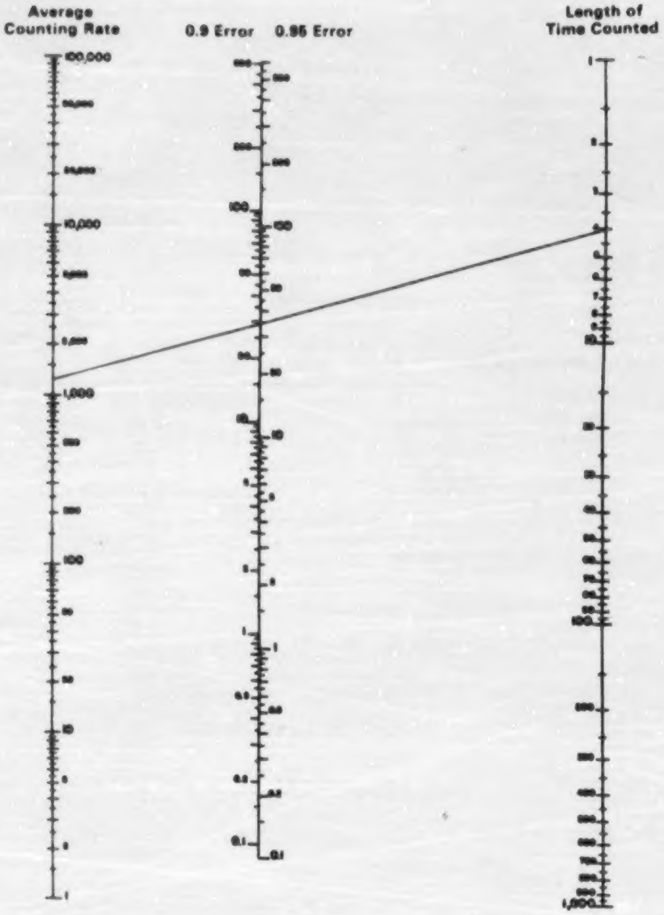
n_s	counting rate of the sample, including the background, in counts per minute.
t_s	number of minutes the sample was counted.
n_b	counting rate of the background, in counts per minute.
t_b	number of minutes the background was counted.

Instructions for Use

Draw a straight line from a point on the left scale that corresponds to the quotient n_s/t_s through the point on the right scale that corresponds to the quotient n_b/t_b ; the point where this line crosses the center scale will correspond to the 0.9 and the 0.95 error of the determination $n_s - n_b$.

APPENDIX 6

ERROR PLOTS AND STATISTICS OF COUNTING



Nomogram for 0.9 and 0.95 Error of Counting Rate Determinations.
(Jarrett, AECU-262, Mon P-126.)

Instructions for Use
Draw a straight line from a point on the left scale corresponding to the counting rate of the sample through the point on the right scale corresponding to the length of time the sample was counted; the point where this line crosses the center scale corresponds to the 0.9 and the 0.95 error of the determination.

Example
The 0.9 error of a sample that averaged 1250 counts per minute during a four-minute determination is 29 counts per minute.

APPENDIX 6

ERROR PLOTS AND STATISTICS OF COUNTING

n	number of counts, one observation
t	counting time, one observation
$\bar{n}$	mean number of counts, series of observations
$\bar{t}$	mean counting time, series of observations
m	number of observations
σ	theoretical standard deviation
S_t	observed standard deviation
S_n	observed mean standard deviation of the number of counts recorded in a preset time
r	average number of counts per unit time interval.

Theoretical Standard Deviation.

1. For Single Observation.

$$\sigma_n = \sqrt{rt} \cong \sqrt{n}$$

2. For Average Number of Counts per Interval.

$$\sigma_{\bar{n}} = \sqrt{rt/m} \cong \sqrt{\bar{n}/m}$$

Observed (Experimental) Standard Deviation.

1. Series of Observations, Preset Time.

$$S_n\left[= \sum_{i=1}^{m} (m_i - \bar{n})^2/(m-1)\right]^{1/2}$$

2. Series of Observations, Preset Count.

$$S_t\left[= \sum_{i=1}^{m} (t_i - \bar{t})^2/(m-1)\right]^{1/2}$$

$$S_n = (n/\bar{t})S_t$$

3. Reliability Factor.

$$R.F. = S_n/\sigma\bar{n}$$

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* Bleuler, E. and Goldsmith, G. J., *Experimental Nucleonics*. Holt, Rinehart and Winston, New York, 1952.

☆GPO 790-662-1977